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**A TEXT BOOK OF
CHEMISTRY**

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A TEXT BOOK OF CHEMISTRY

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PREFACE

The reader who expects in a book on elementary Chemistry just the usual facts and their generally accepted explanations will find them here, stated, it is to be hoped, with adequate lucidity and accuracy. But we have a little more in view. The vast majority of students of Chemistry in schools are not regarding their earliest glimpse of the science as the first stage of their life-work; to them Chemistry is making its contribution with a variety of other subjects to that moulding of the mind which is called Education. It is with that object primarily before us that we have written this book. For that reason an attempt has been made to present a logical and orderly development of the subject. To achieve this is difficult, as every teacher of Science knows. Properly to illustrate and clarify chemical theory requires a considerable knowledge of the actual properties and reactions of chemical substances. Hence there would appear to be a good argument for the acquisition at the outset of as wide a range as possible of chemical facts. But without a background of theory this acquisition is slow and tedious, and we venture to think most practical teachers will agree that the student is best introduced to the theory at an early stage. The use of formulae for example is so helpful that they may well be introduced as soon as possible. We have refused to cut this Gordian knot by putting the theoretical and the descriptive parts in separate sections, and it is hoped that our effort to deal with the difficulty will find favour.

The ultimate dependence of Chemistry upon experiment is duly insisted upon. We have, however, put the practical work in a separate part of the book. The practical details of an experiment present a separate problem, and it makes for clarity and simplicity to keep them to a certain extent apart from the points which the experiment itself is intended to bring out.

We wish to insist that Chemistry is a cultural subject—as much so as Greek or Philosophy—and we have tried to treat it in that spirit. In presenting it we have not felt constrained of necessity to the mere statement of a fact in the dreariest and most matter-of-fact way. The days are gone when dullness was a quality to be counted upon in a school text-book.

The work is intended to cover the scope necessary for, among others, the School Certificate examinations.

For the rest, the book must speak for itself.

It is our desire to pay a tribute to the memory of the late S. E. Brown, M.A., formerly Headmaster of Liverpool Collegiate School, the old Chief and friend of one of us (C. W. R. Hooker).

His books on Elementary Science for beginners have been conspicuously successful, and it was his intention to produce in collaboration with Mr Hooker a sequel, to carry “Chemistry” to a more advanced stage. His untimely death frustrated this project and it has fallen to us to carry it out. In Mr Brown’s Elementary Chemistry the foundations were well and truly laid. Our hope is that the present book will provide a superstructure such as he himself would have approved.

Our grateful thanks are due to the Oxford and Cambridge Schools Examinations Board, the Delegates of the Oxford Local Examinations, the University of Cambridge Local Examinations Syndicate, the University of London, and the Joint

Matriculation Board of the Northern Universities for their kind permission to include some School Certificate questions. We are also indebted to Dr J. F. Spencer and Messrs G. Bell and Sons Ltd. for allowing us to make use of two experiments in Spencer's *Practical Physical Chemistry*, and to Mr F. Fairbrother and Mr D. Ll. Hammick and Mr John Murray for allowing us to make use of experiments in the *Science Masters' Book*.

We have received most generous assistance in the preparation of the plates from Imperial Chemical Industries Ltd., the Editors of *The Industrial Chemist* and the Director of the Science Museum.

The portraits have been reproduced from engravings in the remarkable collection of Mr Reginald B. Pilcher, O.B.E., Registrar of the Institute of Chemistry, to whom we offer our heartiest thanks.

H. A. W.

C. W. R. H.

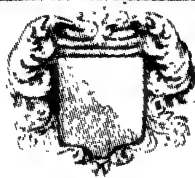
1933



Engraved by J. Smith

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The Honourable



ROBERT BOYLE.

PART I

Chapter I

INTRODUCTION

1. If a piece of clean ironwork be exposed to moist air it rusts and a new ruddy brown substance appears upon it. If we were not so familiar with this simple fact it would probably occasion considerable surprise. Where has this new brown substance come from? Is it modified iron? Does it contain water? A hundred questions might be asked about it. Again, a piece of coal is burnt; it disappears except for some whitish ash quite unlike the original coal. We saw some smoke pass away from it and heat was produced. What has happened? Has the coal been annihilated? If not, can it be reconstructed? An animal builds up its body by feeding entirely upon vegetable matter. From grass to beef is no small step. How has the change taken place? An observer can easily frame for himself endless questions of this sort. Chemistry is the science which sets out to answer them.

Chemistry deals with matter. It is not worth while trying to give a definition of matter; it is one of the fundamental facts of the world we live in. One or two things about it, however, should be noticed.

2. All matter occupies space, i.e. has volume. It also has mass (or weight).^{*} We shall find that in chemistry we have repeatedly to deal with the masses of the substances which take part in or are produced by a chemical change and with their volumes, either in the gaseous state or in solution.

^{*} The distinction between mass and weight does not concern us here. Although in chemistry we deal with the masses of substances, we shall observe the usual custom and speak of the weights.

3. Matter can exist in three forms, *solid*, *liquid*, and *gas*. A *solid*, under any given physical conditions, has a definite volume and a definite shape.* A *liquid* under a given set of conditions has a definite volume, but it takes its shape from the vessel in which it is placed. A *gas* has neither fixed shape nor fixed volume; it always tends to expand so as to fill completely the vessel in which it is placed, and if it is in free space it will expand indefinitely.

4. Chemistry, then, deals with matter. A great many of the questions concerning matter, however, are discussed by the sister science, Physics. The particular tasks of chemistry are the investigation of the composition of matter and of the action and reaction of different kinds of matter on each other.

5. It is necessary at the beginning of the subject to get a clear idea of the difference between a *chemical change* and a *physical* one.

When water is boiled it turns to steam. This is a considerable change. But the steam easily condenses to water again and the change is not permanent. So also when ice melts or water freezes. A piece of dry pipe-clay can be made red hot and when allowed to cool it returns in all respects to its original state. These changes are physical; they are transitory and are easily reversed. Again, corn may be ground to wholemeal flour, a piece of wood may be turned into sawdust, or a piece of salt powdered. Here the change is not easily reversed, but there is no real change in the substance itself. A particle of sawdust is just a small piece of wood; its substance is of essentially the same nature. Compare these changes with the changes involved in the rusting of iron, the burning of coal or the digesting of food. The differences are at once apparent. The substances at the end of these processes are so different from those at the beginning that

* This is true even of a powder; for although it resembles a liquid in taking the shape of the vessel in which it is placed, examination under a microscope shows that a powder is made up of solid particles.

had we not known their origin we would never have suspected it. Who could have guessed that the brown powder, "rust", was produced from the iron, or that a joint of mutton was built up from such materials as grass, clover and water? Anyone, by thinking of the changes going on in the world around him, can find any number of such examples; and his study of chemistry will make him familiar with many more.

As a general guide we may say that when a *chemical* change takes place, at least one new substance is produced, with properties quite distinct from the original substances. When a *physical* change takes place each substance remains substantially the same substance throughout, though its physical properties may be temporarily altered.

6. A *chemical change* is usually accompanied by a *change in temperature*. Three common cases may be mentioned. Firstly, a chemical change may be accompanied by a spontaneous rise of temperature. If a piece of phosphorus in a deflagrating spoon be introduced into a jar of oxygen it quickly bursts into flame and much heat is produced (see § 32). Secondly, a chemical change may require heat to start it, after which it may go on continually; this is what happens when a fire is lighted. Thirdly, a chemical action may require the continuous application of heat. Numerous examples of this will be met with, but it is not always easy to show whether the heat is just a stimulus, or whether any of the heat is actually used up and disappears in the course of the action. As a matter of fact, heat does actually disappear in many such cases.

7. When chemical changes occur, some substances disappear and other substances are formed. Frequently two substances can be made by the splitting up of one, and the question arises as to how far this process can be carried. When by splitting up substances we arrive at a substance which appears to be really a simple body, incapable of being resolved further, it is called an "element". There are about eighty elements known, and of these

all the material substances in nature are constructed. Though the essential fact about an element is that it has never been split up into simpler substances, there is strong reason to believe that the elements are really fundamental substances and that it is not just our inability to resolve them further that makes them appear so.

8. An *element*, then, is a substance which has not been decomposed by the ordinary processes of chemistry into simpler substances (see § 125, footnote). Elements are united chemically to form *compounds*. The word "chemically" here should be specially noted. Merely mixing together the ingredients is not enough. Candle-grease, for example, consists of carbon (charcoal) combined with an invisible gas, hydrogen. But carbon and hydrogen just placed together clearly do not make candle-grease.

9. The chemist makes an important and fundamental distinction between a *mixture* and a *compound*. When different substances, whether elements or compounds, are mixed together usually nothing special happens. The substances may be mixed in any proportions and no heat is produced nor is there any other evidence of chemical action. We are then dealing with a *mixture*.

If, however, a *compound* is formed, the following facts are noticed:

(I) The *compound contains the elements* of which it is made in strictly *definite proportions by weight*. Hence, if the compound be made directly from its elements, unless the quantities are carefully chosen, there will be some of one or other of the ingredients left unchanged at the end.

(II) It is impossible to recognise in a compound the original constituents in the final substance, nor can they be separated without a chemical action.

(III) The formation of a compound from its elements or from simpler compounds is a chemical change, and hence there will be

a *change in temperature*. In forming a *mixture* from its ingredients no change in temperature is observed.

10. The "impurities" so often found in a chemical substance usually form a mixture with it. Anything other than the substance itself must be regarded as an "impurity". They are usually harmless and unimportant, as for instance a little moisture in many salts, or a little silica in substances of mineral origin. They become important sources of error, however, when we are dealing with accurate quantitative weighing. It may be a little consolation to the beginner to be told that an inaccuracy in his results may be due to this cause and not to his own lack of skill. In any really important investigation a large part of the preliminary work will probably consist in the preparation of the substances to be investigated in a sufficiently pure condition.

11. But whatever physical or chemical changes matter may undergo, the *total amount of matter present never alters in the slightest degree*. As an example to illustrate this the following experiment will serve.

A large test-tube, a much smaller one and a rubber stopper to fit the larger test-tube are required. In the large tube place a little solution of ordinary salt. In the smaller put some solution of silver nitrate and place the small tube inside the large one, keeping the solutions separate, as in fig. 1. Stop up the outer tube and weigh. Now gently tilt the tubes so that the liquid is spilled from the inner tube and the two solutions are mixed. A thick white precipitate is formed owing to the chemical action between the two solutions. Weigh again and note that there is no change in the total weight, though a marked and obvious chemical change has taken place.



Fig. 1. Chemical action without change of weight.

12. The point may be further illustrated by the following experiment. Place some moist iron filings in a glass globe like

that in fig. 2. Seal off by heating the opening *A*. Weigh the whole and lay aside for a day or so. When the filings are seen to have rusted weigh the whole again. The total weight is found to be unaltered. Now break off the sealed point and weigh again, not forgetting to include the piece broken off. The weight will be found to have increased. Rusted iron is heavier than the same iron before rusting. The iron has taken something from the water and air around it and the gain in its weight is exactly equal to the loss in weight of the air and moisture. Hence there is no change in the weight of the whole so long as the bulb remains sealed. When the vessel is opened there is a slight inrush of air and the outside air mixes with the air inside, which soon becomes normal again. At the second weighing the iron, now rusted, is heavier than at the start and the air weighs what it did originally. So on the whole there is an increase.

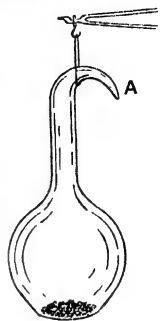


Fig. 2. Chemical action without change of weight.

This experiment needs to be done carefully, as the increase in weight is small. A small quantity only of iron filings is required. Since the filings take something from the air in rusting, it is only to be expected that a limited quantity of air cannot rust more than a limited quantity of filings.

13. The point which these experiments illustrate, that whatever chemical changes occur the total amount of matter present never varies, is called the *Law of the Conservation of Mass* or the *Law of the Indestructibility of Matter*. The former phrase is better. Matter might be indestructible and yet it might be possible to create it. The principle is so well established now that its acceptance is almost second nature. Yet it has required a good deal of research to verify it. And when demonstration has shown that matter is never destroyed it still has to be shown that it cannot be produced. If we watch a plant grow, surely the most obvious conclusion to come to is that here we are dealing with a gradual

creation of matter. It is only after long and careful observation and experiment that the definite conclusion is arrived at that the plant gets its material from the air and the soil and that the apparent production of matter is the veriest illusion, as great an illusion as it is that the sun goes round the earth.

14. Whilst referring to the Law of the Conservation of Mass it is as well to notice something about the use in science of the word "Law". A law in chemistry, or in science generally, is in one respect exactly the opposite of a law as a lawyer understands it. In human affairs Parliament in its wisdom decides a thing ought to be done and then passes a law to say that it shall be done. Whether it *is* done is another matter. The law may be broken or ignored. But in science, the scientist first finds out by investigating what happens and then frames the law afterwards. If the politician's law is not obeyed the law-breaker is brought to account. But if a scientific law is disobeyed the law-maker is brought to account. In human affairs if a man breaks the law he is called upon to amend his ways. In science, if any phenomenon breaks the law it is the law-framer, the scientist, who is called upon to amend his ways and frame the law so that it will not be broken. An inaccurate man frequently takes refuge in the proverb "The exception proves the rule". But he misses the point of the adage. A better phrase would be "The exception probes the rule". It tests it. And either the rule must be revised and restated so that the exception is an exception no longer or there is no rule at all. Parliament makes laws; a scientist discovers them.

Chapter II

HISTORICAL

15. The modern science of chemistry is the result of a combination of two historical ingredients. The ancient Greeks were very fond of discussing things, and so far as words went they showed great ability. To them chemistry was a part of philosophy. The practical and experimental side of the subject was almost entirely ignored. At a later date, from the beginning of the Christian era up to the seventeenth century, there were the alchemists. Alchemy was a mixture of practical chemistry and magic. In sharp contrast to the philosophers they were essentially experimentalists. But their work was usually undertaken with a limited and defined end in view, the two chief aims being the artificial manufacture of gold and the production of the "elixir of life", which was to keep men from death. These gradually gave place to investigations of the action of drugs on the human body and to the preparation of new substances for use in medicine. A large number of substances were discovered and their action on one another was investigated.

16. We can, however, learn from the alchemists two things to avoid. They groped about without any established fundamental principles. Such principles as they worked on were frequently wrong, and they could have been proved wrong had they been thoroughly investigated. Then again, they worked from the very start to a definite end, such as the conversion of the baser metals into gold. The real success of modern science is due to men who started at the beginning and who patiently and carefully explored each region and then went on to the next with no more definite end in view than the discovery of truth. Now that a large field has been investigated in this way we can tackle

definite problems with reasonable hope of success, and we can also frequently judge whether a problem is ripe for solution or not. It is interesting to note that the alchemists thought the manufacture of gold from ordinary substances a reasonable problem to tackle; the advance of chemistry, however, convinced men fifty years ago that this was utterly impossible. The view is shifting again. In a few rare cases, under very special conditions and in minute quantities the change of one element into another has been effected. The alchemist's dream is still far, very far, from being realised. Yet it would be rash to assert confidently that artificial gold can never be produced, though even if it were, all the evidence is that it would only be by a very difficult and expensive process and that it could never be made in anything but microscopic quantities. We could, however, never have got even remotely within sight of this success had we not first turned right away from the alchemists' methods.

17. The two streams—the philosophers and the alchemists—meet in Francis Bacon,* Queen Elizabeth's famous Lord Chancellor. He was a great philosopher and his work, *Novum Organum*, shows, too, a clear appreciation of the value of experiment.

Bacon's life was far too full to allow him time for much experimental research himself, but his attitude to the philosophers who argued but did not experiment or investigate is well shown in the following extract from his writings:

“In the year of our Lord 1432, there arose a grievous quarrel among the brethren over the number of teeth in the mouth of a horse. For thirteen days the disputation raged without ceasing. All the ancient books and chronicles were fetched out, and wonderful and ponderous erudition, such as was never before heard of in this region, was made manifest. At the beginning of the fourteenth day, a youthful friar of goodly bearing asked his learned superiors for permission to add a word, and straightway,

* Francis Bacon (1561–1626). The reader is strongly recommended to read Macaulay's very interesting essay on this remarkable man.

to the wonderment of the disputants whose deep wisdom he sore vexed, he beseeched them to unbend in a manner coarse and unheard-of, and to look in the open mouth of a horse and find answer to their questionings. At this, their dignity being grievously hurt, they waxed exceedingly wroth; and, joining in a mighty uproar, they flew upon him and smote him hip and thigh, and cast him out forthwith. For, said they, surely Satan hath tempted this bold neophyte to declare unholy and unheard-of ways of finding truth contrary to all the teachings of the fathers. After many days more of grievous strife the dove of peace sat on the assembly, and they as one man, declaring the problem to be an everlasting mystery because of a grievous dearth of historical and theological evidence thereof, so ordered the same writ down".

Chemistry, like all other branches of Science, has made rapid progress through the development of an adequate theory and the testing of every inference by careful experimental work. It may be said to have started on its real success as a science with the acceptance of Dalton's* Atomic Theory and of Avogadro's† Law of Gases, on the theoretical side, and with the use of the chemical balance, on the practical side.

18. It cannot be too firmly fixed in the mind of the student that *chemistry is essentially an experimental science*. Every casual fact mentioned in this book has only been found out by experiment, often prolonged and repeated experiment. Such a statement as "Sulphur boils at 444.5°C .", or "The specific gravity of iodine is 4.9", means that someone has done the necessary experimental work. Life is too short for every student to work over the whole field for himself. Yet it must never be forgotten that it is always by means of experiment that new ground is broken and new territory conquered.

Chemistry is one of the "Natural Sciences"—the sciences

* John Dalton (1766–1844), physicist, chemist, meteorologist and naturalist, founder of the Atomic Theory. See also chaps. III and XII.

† Amadeo Avogadro (1776–1856), physicist, of Turin. See also chap. VI.

which discuss the physical world about us. Natural sciences deal with the real material things of our experience. Once the student has grasped exactly what the scope of chemistry is, he will realise its enormous range of application and be willing to agree that it is probably the most important of the "Natural Sciences". Practically all the others come to it for help. The doctor, the zoologist, the physiologist, all require information about the material changes which are constantly taking place in the body of a man or an animal, information which only the chemist can supply. The closeness of the link between the chemist and the doctor is seen in the popular use of the name "chemist" to describe a man whose business is with medicines, and who is more properly called a pharmacist or an apothecary. In French and German there is no such confusion in the use of the word "chemist". The botanist requires similar help as he considers the chemical changes in plants. The geologist and the mineralogist, too, depend largely on the chemist, who tells them how to find out the composition of rocks and minerals and helps them to consider the chemical actions in nature which have made the earth's crust as it now is.

Turning to the practical business world, nearly every kind of technical operation requires the service of trained chemists. The manufacturers of soap, steel, glass, textiles, coal gas, candles, sugar, matches and a hundred and one other things all need expert and specialised chemists on their staffs. The entire trade in artificial dyestuffs has been brought into existence by chemists, starting with coal tar.

Chemists invented and produced all the ammunition used in the Great War, and also the bulk of the medicines and practically all the antiseptics and anaesthetics for the treatment of the wounded. An army of chemists is of necessity kept busy on the food supplies of our vast urban populations, separated as they are so often from the sources of supply by hundreds of miles in space and by months in time.

The subject has become so vast that no one man can possibly be familiar with it all. This book deals with those fundamentals which chemists of all kinds must know. The subject cannot fail to interest. So many of the phenomena are curious and interesting of themselves; the practical work gives scope for much skilful manipulation at which the Anglo-Saxon race is particularly adept; the theoretical knowledge obtained is a wonderful monument to human genius and human patience. The subject bears closely on actual affairs and can be made to lead to a useful and successful life work, and its study provides a first-rate mental discipline. It is an excellent training, too, for the powers of observation, a point which anyone interested in the "Scout" movement will fully appreciate. It teaches the blending of theory and practice and hence the cultivation of powers of judgment. This may make a lasting impression on the mind even when the memory of the actual facts studied in the cultivation has grown dim. This, perhaps, is the most important intellectual result of true education. On the moral side, the practice of rigidly testing theory against fact makes impossible the habit of accepting shams and half-truths—a habit so common among badly educated folk to-day.

Chapter III

THE GAS LAWS

19. The common properties of a gas as such—its density, its elasticity, the way its volume changes when the pressure or temperature are altered, and so on—are really questions for the physicist to discuss. It is essential, however, for the chemist to know a good deal about them. So the present chapter is important.

We have seen that a gas always expands so as completely to fill the vessel in which it is contained. This expansion is practically instantaneous. The vessel prevents the gas from expanding further, but the tendency to go on expanding is shown by the pressure on the inside of the vessel. If the vessel be expansible—as, for example, a toy balloon—it expands under this internal pressure, until the force exerted by the container, tending to contract, balances the pressure of the gas inside and there is equilibrium. This *pressure* is an important physical quantity. If we want to know how much of a gas we are dealing with, obviously a knowledge of the *volume* alone gives no help, since any amount of a gas will expand to fill a given volume. But if a small quantity of gas be introduced into a space it will clearly exert a smaller pressure than would a larger quantity in the same space. As a fixed quantity of gas expands in volume its pressure gets less. Thus the volume and pressure of a mass of gas vary in opposite directions. If the temperature be kept the same, the law is that the *volume varies inversely as the pressure*, or P being the pressure and V the volume, *the product PV is constant*. This law, which the reader will test experimentally in his study of physics, is known as **Boyle's* Law**, and it is sufficiently accurate for our purposes, though it is in fact not quite exact.

* The Hon. Robert Boyle (1627–91) was an Irishman. He is usually described as “The Father of English Chemistry and the uncle of the Earl of

20. The pressure is usually measured in millimetres of mercury. If one side of a U-tube of mercury be connected to a closed container of gas (see fig. 3) there will ordinarily be a difference of level of the two sides of the tube. The difference in level measures the difference between the pressures on the two sides. That on the open side is the pressure of the atmosphere, and is read by an ordinary barometer in millimetres of mercury. As the atmospheric pressure varies from day to day and from place to place, this must be read for each experiment. This reading plus the height AB in millimetres gives the pressure in the bulb X . If the height in the limb connected with X is higher than the open limb, the difference in height must be subtracted from the barometer reading. In such a case the pressure of the gas is *less* than the atmospheric pressure. The average height of the barometer at sea-level is about 760 mm. and the pressure measured by 760 mm. of mercury is the standard normal pressure at which gas volumes are reckoned.

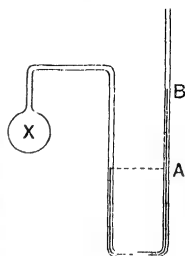


Fig. 3.

21. Boyle's Law can conveniently be verified by using a graduated glass tube in the form of a J with the shorter arm sealed (see fig. 4a). Mercury is poured into the longer and open arm and the volume V of air enclosed is measured by means of the graduations on the tube. The pressure P of the enclosed air is the height AB plus the barometric height. By varying the amount of mercury, different corresponding values of P



Fig. 4 a. Boyle's Law Apparatus.

Cork". He was one of the founders of what eventually became the Royal Society, the fellowship of which (F.R.S.) is perhaps the most coveted of British scientific distinctions. He was much interested in Christian missionary work. His famous law is sometimes called Mariotte's Law, though Mariotte only formulated it some seven years after Boyle.

and V can be found. The product $P \times V$ is calculated and is found to be the same for each observation.

A more convenient form of the apparatus is shown in fig. 4*b*. In this apparatus the amount of mercury is not altered. The glass tube is in two parts connected by a tube of rubber and the pressure is varied by raising or lowering the open glass tube which slides up and down a scale. The difference in the heights of the two sides is read and the calculation made as before. This apparatus is more convenient, as the trouble of pouring mercury in and out is avoided.

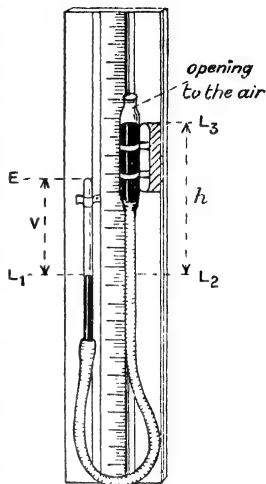


Fig. 4*b*. Boyle's Law Apparatus.

22. The atmospheric pressure varies from time to time, and so the pressure of a gas when the volume is measured in an actual experiment is usually not exactly 760 mm. of mercury. It is then necessary to calculate the volume that it would occupy at the standard pressure of 760 mm. for purposes of comparison with other gases and the results of other experiments. By the aid of Boyle's Law this calculation is easily made. For instance, 46.1 c.c. of a gas are collected and measured at a pressure of 754 mm. of mercury. What would be the volume at 760 mm.?

Let V be the required volume. Then by Boyle's Law the product of pressure and volume is constant, i.e.

$$760 \times V = 754 \times 46.1,$$

$$V = \frac{754 \times 46.1}{760} = 45.7 \text{ cubic centimetres or } 45.7 \text{ c.c.}$$

* The student who uses logarithms will do well to notice and remember that $\log 7.60 = 0.8808$.

23. Practically all substances expand on heating; the expansion of a gas is much larger than that of a liquid or a solid. If the expansion be prevented by the space being confined, then the pressure rises. Hence before a volume of gas gives us a correct idea as to how much gas is present we must know the *temperature*. If we ignored the change in temperature when it rose, the increased pressure of a given confined volume of gas would give the impression that the amount of gas present was greater than it really was.

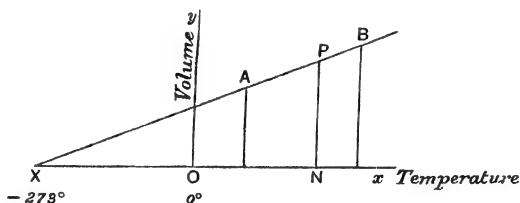


Fig. 5. Relation between Volume and Temperature.

If a fixed quantity of gas be heated, the pressure being kept constant, and a graph be drawn plotting the volume against the temperature, a diagram is obtained like that in fig. 5. Suppose AB is the part obtained by actual observation. This is found to be a straight line. Produce AB to meet the axis of x at X . Then by the laws of similar triangles $\frac{PN}{NX}$ is the same for all points P on BX . The point X is found by experiment to correspond to -273°C . and to be the same for all gases. We usually measure the temperature from the freezing-point of water, which is a purely arbitrary point. There is no reason but our convenience for choosing this point. Supposing we choose—keeping the degree centigrade unaltered—to measure temperatures from X as origin instead of from O . All our temperatures are then measured by a number 273 more than before. These are called “Absolute Temperatures”. We have, then, that the volume of a gas at

constant pressure is proportional to the absolute temperature, that is, to the centigrade temperature plus 273°. This statement is known as **Charles' Law**.

24. If a space contains mixed gases, the total pressure may be calculated by supposing that each gas occupies the whole of the space and then adding together these "partial pressures" to get the total pressure. The law that the *total pressure is the sum of the partial pressures* is due to Dalton. One application of it is of special importance to the chemist. Frequently a quantity of gas is collected and its volume measured in contact with water. Now water easily evaporates and there is always vapour present over water. It is found that if water is allowed to evaporate into a space it goes on doing so until the vapour exerts a certain definite pressure, which depends only on the temperature. For instance, at 16° C., an ordinary room temperature, it is about 13 mm. of mercury. Hence if a gas be collected at 16° C. in contact with water, and its volume and pressure noted, 13 mm. of the pressure are due to aqueous vapour. 13 mm. are therefore subtracted from the observed pressure and the difference is the pressure due to the gas. *This point must never be forgotten when calculating the amount of a gas collected over water.*

A table giving the maximum pressure or "tension" of aqueous vapour for ordinary temperatures follows:

Temp. ° C.	mm.	Temp. ° C.	mm.	Temp. ° C.	mm.
0	4.6	9	8.6	18	15.5
1	4.9	10	9.2	19	16.5
2	5.3	11	9.8	20	17.5
3	5.7	12	10.5	21	18.6
4	6.1	13	11.2	22	19.8
5	6.5	14	12.0	23	21.0
6	7.0	15	12.8	24	22.3
7	7.5	16	13.6	25	23.7
8	8.0	17	14.5		

Chapter IV

OXYGEN

25. The laws of chemistry will be more fully appreciated after some acquaintance with actual chemical substances. It should be noted, however, that the distinction in the popular mind between chemical substances and other substances is quite artificial. Every substance is a chemical substance. We shall confine our attention at first, as a matter of convenience, to those which are fundamental or simple and so lead on to more complicated compounds, paying special attention to those which are useful or specially interesting.

26. **Oxygen**, being the most abundant element in nature and entering as it does into all the most important chemical processes of our daily life, will be the first element to claim our attention. Oxygen is a colourless gas. It was first discovered by the Rev. Joseph Priestley (1733–1804) in 1774, who prepared it from a red powder we call mercuric oxide (see § 30).

A number of substances when heated give off oxygen, and in the laboratory it can conveniently be made thus from *potassium chlorate* (see § 600).

A hard-glass test-tube is required. An ordinary test-tube is too soft to stand the necessary heating. Place some of the crystals of the chlorate in the tube and heat strongly in the Bunsen flame. The crystals melt and effervesce, a gas is given off and a white amorphous mass of potassium chloride remains. The gas is oxygen. In the first stages of this process of preparation some potassium perchlorate is found, which, however, breaks down into potassium chloride and oxygen as the heating proceeds. The gas comes off more freely and easily and at a lower temperature if a little manganese dioxide is mixed with the

potassium chlorate. The manganese dioxide remains unaltered and appears to take no part in the action. The potassium chloride can be dissolved away and the manganese dioxide recovered unchanged by filtering. When the manganese dioxide is used there is no intermediate formation of perchlorate. A substance whose presence facilitates a chemical action without itself being altered is called a "Catalyst" or a "Catalytic Agent". Such catalysts are of special importance in many technical processes and further examples will be met with in the present book (see §§ 169 and 351).

27. The gas is only slightly soluble in water and can be collected over water in a gas jar by the aid of a pneumatic trough and a beehive shelf (see § 598). A "pneumatic trough" is a high-sounding name which merely means a dish a few inches

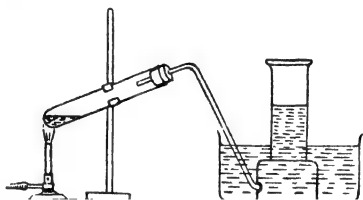


Fig. 6. Preparation of Oxygen.

deep—an ordinary pie dish will serve the purpose quite well. The beehive shelf is a shallow cylinder of earthenware, closed at the top except for a fairly small hole in the middle and with an opening at the side to allow of the passage of the tube delivering the gas. The shelf is placed in the trough and entirely covered with water, and a gas jar full of water and inverted stands over the beehive shelf (see fig. 6). The gas is bubbled through the water into the gas jar and when the latter is nearly full a glass plate is slipped over the mouth and the jar of gas removed. This simple apparatus is used for collecting gases which are insoluble or not very soluble in water. Sometimes, when the gas to be

collected is somewhat soluble in cold water, hot water is used (e.g. nitrous oxide, see § 296), as the solubility of a gas decreases rapidly with the rise of temperature.

28. A modification of this scheme is employed when a gas is to be collected over mercury. The modification is necessary as mercury is expensive and there is usually only a limited supply available. So the trough is made smaller, no beehive shelf is used, but the bottom of the trough is raised at one end except for a groove which divides the raised end into two parts. The gas jar containing mercury is placed over the groove and the tube carrying the gas is passed along the groove under the gas jar. This economises space and diminishes the amount of mercury required.

29. A number of other substances give off oxygen when heated, such as silver oxide, mercuric oxide, etc., many peroxides (see § 463), such as lead peroxide, manganese peroxide, barium peroxide, chromium peroxide, etc. Some salts such as nitrates, chlorates and iodates also evolve oxygen on heating. It is also produced by the electrolysis of certain dilute acids and salt solutions (see chap. v).

30. The production of oxygen from mercuric oxide is of great historical interest. It was by heating this compound that Priestley first prepared oxygen (see § 26). He communicated his discovery to Lavoisier,* who used it both to prepare oxygen and to prove its presence in air. He heated mercury in a retort, the open end of which dipped into mercury. The heating was continued for over a week. At the end of the time, on cooling, the mercury passed up into the retort and the space over the mercury was diminished by one-fifth of its volume. No further

* Antoine Lavoisier (1743-94) was a Frenchman who has considerable claim to be regarded as the founder of modern chemistry. He was guillotined during the French Revolution, an appeal for his reprieve being dismissed on the plea that "The Revolution has no need of chemists". A similar contempt for men of culture has been shown more recently in the Russian Revolution.

heating could reduce this space any more. At the same time the mercury was seen to become tarnished, and particles of a red powder appeared upon it. The red powder is a compound of mercury and oxygen, mercuric oxide. On heating this oxide to a much higher temperature it splits up again into oxygen and mercury, and in this way Lavoisier recovered a volume of oxygen equal to the loss of volume of the air in his retort when he prepared the mercuric oxide. This showed that oxygen was a constituent of the air to the extent of one-fifth of its volume.

31. Sodium peroxide gives off oxygen when it reacts with water at the ordinary temperature of the laboratory. This is a convenient source of oxygen, as no heat is required. The practical laboratory details are given in § 599. The method may be modified so that the action can be stopped by the pressure of the oxygen generated as soon as the gas ceases to be drawn off.

Sodium peroxide in its most familiar form is a light yellow powder, but for the present purpose it is melted and solidified into compact rectangular lumps. Each lump is enclosed in a sealed metal container and the oxide is sold in this form under the trade name of "oxone".

A simple form of the apparatus is shown in fig. 7. The bell jar, *B*, open below and corked at the top, stands in a deep vessel of water and is raised just above the bottom of the vessel. The sodium peroxide is placed on any convenient small stand so that it is raised up well inside the bell jar. A delivery tube passes through the cork and can be clipped at *X*. The oxone container is punctured in one or two places when required for use. On opening the clip *X* water passes into *B* and acts upon the oxone, oxygen being evolved and drawn off at *Y*. If the clip at *X* is closed at any

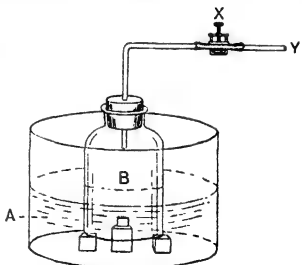


Fig. 7. Preparation of Oxygen from "Oxone".

time, oxygen collects in *B* and drives out the water, leaving the oxone high and dry, when the action ceases. In this way oxygen is only generated so long as it is being drawn off. The principle may be recognised as that of the ordinary acetylene bicycle lamp. It is substantially the same as Kipp's apparatus described later in connection with the preparation of hydrogen (fig. 8) (see § 48).

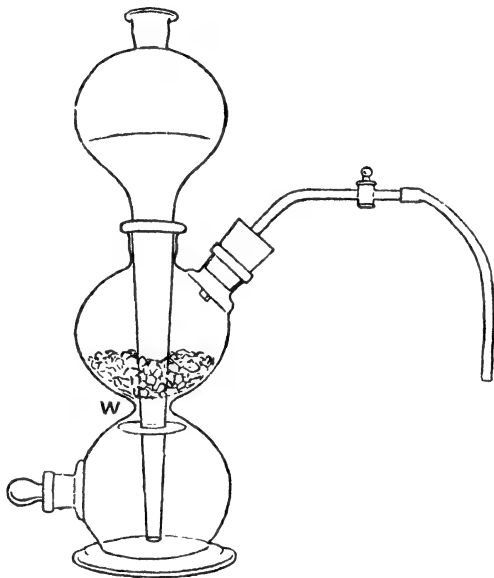


Fig. 8.

32. By far the most striking property of oxygen is its power of supporting combustion. This is conveniently shown by the aid of a deflagrating spoon, a small spoon or cup on the end of a stiff wire passing through a metal disc (see fig. 9).

If a piece of phosphorus be placed in the spoon, which is then inserted in a jar of oxygen, the phosphorus catches fire and burns very brightly. A glowing splinter or a piece of red-hot charcoal

placed in oxygen at once bursts into flame. All the substances which ordinarily burn in air—sulphur, wood, a piece of candle, etc.—burn in oxygen readily and brilliantly. This power of supporting and accelerating burning is the most characteristic property of oxygen and is used to identify it. A glowing splinter is dipped into the gas as a test.



Fig. 9. Deflagrating spoon.

There is only one other common gas, nitrous oxide (see § 296), which supports combustion in this way. The most obvious distinction between the two gases lies in the fact that oxygen is completely used up during combustion, and if the product of the combustion be removed no gas remains. If, for instance, a piece of ignited sulphur be placed in a small cup floating on water and a jar of oxygen be placed over it, the sulphur burns vigorously, the product of the combustion dissolves in the water and the water ascends and, if the oxygen was pure, fills the jar. If this same experiment be performed with nitrous oxide there is as much gas left afterwards as before. Unless care is taken some of it may escape, as the heat causes it to expand and to bubble out of the jar.

33. Compounds of a substance with oxygen are called oxides. An oxide consists of two elements only, oxygen and the element of which it is the oxide. The syllable “-ide” as a termination is for the most part used in this way in chemistry. It denotes a compound of two elements only. Thus, copper sulphide is a compound of copper with sulphur alone, calcium carbide of calcium and carbon alone, and so on. It is a great help if the name of a substance can give at once some idea of its composition, and a good many similar points of nomenclature will be met with (see § 149).

34. Many metals burn readily in oxygen to produce oxides if they are in the form of filings or ribbon. Magnesium, aluminium and zinc burn with a white light, forming in each case the oxide

of the metal. A piece of steel watch-spring, heated to redness, catches fire and throws off many sparks. The oxide produced is called magnetic oxide of iron, as it is attracted by a magnet, whereas other oxides of iron are not. Sodium, potassium and calcium all burn very readily in oxygen, the two former giving peroxides.

35. We have seen that sulphur, phosphorus and charcoal (carbon) all burn brightly in oxygen. If the burning takes place in a jar with some water in it, the substance formed reacts with the water to produce a new compound. If a little blue litmus solution be dropped into the solution it at once turns red. In the case of the phosphorus, it turns bright red and remains so. The sulphur also yields a bright red. In the case of the carbon the change to red is not very sharp; the litmus acquires a port wine colour.

Substances which redden blue litmus are called **acids**; they are a very important class of compound (see §§ 142 and 625). It was the power of yielding acids in this way which gave oxygen its name. The name means "acid-producer". It is not at all a good name. Many substances when burned in oxygen do not yield acids in the presence of water, several acids contain no oxygen. The essential ingredient in an acid is not oxygen but hydrogen.

36. We have seen that Lavoisier discovered that about one-fifth of the air was oxygen. This may now be shown in a number of ways which are simpler than his. If a piece of burning sulphur be floated on a cork in a trough of water and a gas jar containing air be inverted over it, the oxygen of the air combines with the sulphur, the gas produced dissolves and the water rises and fills one-fifth of the jar (see fig. 10).

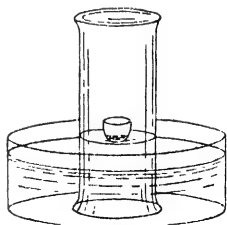


Fig. 10. Burning Sulphur in Air.

This may be done more accurately with a piece of phosphorus

and a graduated tube as in fig. 11. The phosphorus is introduced into the tube and kept in place by a wire as shown. Slow oxidation takes place and when the cork is removed with the end of the tube under water the water enters the tube and the contraction of the space is measured on the graduations. It will be found that after 21 per cent. of the air has been removed no further contraction will take place (see § 622). The air that remains is now incapable of supporting combustion and a lighted match or taper put into it is immediately extinguished. This inert gas remaining is called "nitrogen".

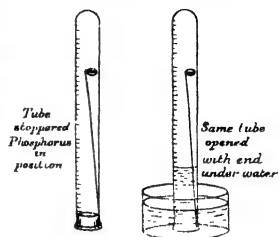


Fig. 11. Composition of Air—by Phosphorus.

37. The question naturally arises: Is the oxygen present in the air in a combined state, or is it just mixed with the nitrogen? The simplest way to test this is to replace the oxygen and see what happens. If the correct quantity of oxygen—prepared, say, from potassium chlorate as above—be passed into the inert gas obtained by removing the oxygen from the air, the resulting mixture is a gas which cannot be distinguished from air. Also there is no evidence that a chemical change takes place when it is introduced, and in particular there is no rise in temperature. This suggests that **air is a mixture**. Further evidence is provided by the fact that oxygen can be extracted from the air by purely physical means. Air is not very soluble in water, but it is to a certain extent. If tap water be boiled, a certain amount of air can be driven off from it. If this air be collected and the oxygen removed by phosphorus, it is found to contain a larger proportion of oxygen than ordinary air. Again, air can be liquefied by applying great pressure and at the same time lowering the temperature. Liquid oxygen boils at -183°C. , a higher temperature than the boiling-point of the other constituent, nitrogen (B.P. -195°C.). Hence, if liquid air be allowed to evaporate, the oxygen is less

volatile than the rest and the gas which comes off consists of only about one-seventh oxygen instead of one-fifth, the residue containing a larger percentage of oxygen than before. This has been made the basis of a scheme for separating oxygen and nitrogen from the air, which scheme is now the source of most of the oxygen used for commercial and technical purposes.

Another piece of evidence that air is a mixture is that the properties of air are what would be expected from the properties of the constituents. Nitrogen being quite inert and oxygen a strong supporter of combustion, the power of supporting combustion exhibited by ordinary air is just as might be anticipated if air is a mixture. It has already been noticed that when two substances combine chemically there is usually no similarity at all between the properties of the final compound and of its components.

38. Oxygen can also be obtained from the air by heating barium oxide. It combines with oxygen and becomes barium peroxide, which on greater heating gives off oxygen and becomes barium oxide again. This used to be employed as a commercial method (the Brin Process), in which, however, it was the temperature which was kept constant, at about 700°C ., while the pressure was varied. On raising the pressure the peroxide was formed, on decreasing it the peroxide turned back to the ordinary oxide and oxygen. The liquid air method has superseded this.

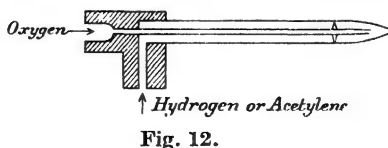


Fig. 12.

39. Commercially oxygen is sold in steel cylinders containing the oxygen under pressure. It was formerly much used for lime-light, in optical (magic) lanterns. A small cone of lime was heated to incandescence by a stream of coal gas or hydrogen burning with

a supply of oxygen. The burner used is shown in fig. 12. It is also used in oxyacetylene welding. Oxygen and acetylene (a compound of carbon and hydrogen) are burned together and give a very high temperature.

40. Oxygen not only supports combustion; it also supports life. The blood owes its colour to a substance containing iron, called haemoglobin, which has the power of combining with oxygen to form oxyhaemoglobin. This it does in the lungs, and the bright red "arterial" blood flows from the lungs to the left side of the heart, whence it is pumped through the body, along the blood vessels and back to the right side of the heart. On its journey the oxygen of the oxyhaemoglobin combines with the waste carbon compounds in the tissues. The carbon dioxide thus produced combines again with the haemoglobin and is taken round to the right side of the heart as venous blood. This venous blood is of a darker and more purple hue. From the right side of the heart the blood is passed round the lungs, where oxygen from the air replaces the carbon dioxide and the latter is breathed out. It will be noticed that an essential part of this process is the power of the oxygen to displace the carbon dioxide. If a gas be breathed which is capable of forming a compound with the haemoglobin more stable than the oxyhaemoglobin, so that oxygen is not capable of decomposing it, the result is serious and may be fatal. Several poisonous gases—notably acetylene and carbon monoxide—owe their lethal properties to this. Coal gas contains carbon monoxide and hence is dangerous.

41. Pure oxygen is often administered to patients suffering from diseases which impede the functions of the lungs, such as pneumonia; its usefulness in such cases is not very great. It is frequently stated that if pure oxygen be breathed the result is intoxication followed by exhaustion from the materials of the tissues being burned up too fast. This is an exaggeration. The blood normally takes up nearly as much oxygen as it can hold chemically, and the substitution of pure oxygen for air does not

greatly increase this. It has been proved, however, by experiments on animals, that under pressure the blood can take up a good deal more oxygen, so much so that the effect of removing a great deal of blood may be counteracted in this way. Aeronauts are supplied with oxygen when they are ascending to great heights, and with this help aeroplanes have been flown up to 40,000 ft., where the air is so rare that ordinary breathing becomes impossible, as the pressure of oxygen is so small.

42. The familiar processes of decay are due for the most part to oxygen, which is thus the scavenger of nature. The process is chemically the same as burning, but slower. Occasionally the rise in temperature produced is considerable. If a pile of stale wet grass be opened up it will be found to be quite hot and reeking inside. The decay is progressing so quickly that "slow combustion" is taking place. Occasionally such things as hayricks catch fire from this cause. The phosphorescence seen sometimes on a piece of stale fish is due to slow oxidation.

Chapter V

HYDROGEN

43. We will now turn our attention to another elementary gas, **hydrogen**. This is a very light and inflammable gas, first discovered by Henry Cavendish (1731–1810).

In the case of oxygen there are, as we have seen, a considerable number of substances available which contain oxygen in combination and which readily decompose on heating, giving off the oxygen. There are, however, no familiar compounds of hydrogen which yield this gas on heating, so the preparation of hydrogen is effected in quite a different way. The commonest laboratory method of preparing it consists in displacing the hydrogen from a suitable compound, usually by a metal. There are cases, however, as we shall see, in which hydrogen can be obtained from certain of its compounds by directly splitting them up, but in these cases the splitting up is usually done by an electrical method.

44. Many of the bottles in a laboratory are labelled **acids**—sulphuric acid, hydrochloric acid, acetic acid and so on. These acids will be described later, both as a class and singly (see §§ 142 and 625). The reader has already been told that all acids contain hydrogen. Water also contains hydrogen, being in fact a compound of hydrogen and oxygen, i.e. an “oxide” of hydrogen.

45. Again, the word **metal** is used a good deal in chemistry. For the moment, it can be taken that the chemist and the plain man agree in calling such common substances as iron, tin, zinc, copper, etc., metals, provided they are elements and not mixtures or compounds. Thus a chemist would not call brass or pewter a metal, as they are both mixtures. Such mixtures are called “alloys”. The chemist, however, also calls, in addition, a number

of other elements "metals"—such as sodium, potassium, calcium, etc., which do not obviously resemble the familiar metals. A discussion of the precise meaning of the word "metal" as used in science must be postponed until later (see § 504).

46. Certain metals will easily displace the hydrogen from water or from an acid. In such cases the hydrogen is liberated and the metal takes its place and forms a new compound. Let us then turn to a few actual cases (see §§ 602 and 604).

The most active metals will at once replace the hydrogen from cold water. The commonest of such metals are sodium, potassium and calcium. Sodium and potassium react so readily with water or moist air that they are usually kept under petrol or naphtha, which contain no oxygen. In the case of potassium the action is so vigorous that if air is present the hydrogen produced catches fire. Calcium acts more slowly.

A piece of sodium is wrapped in filter paper and slipped into an inverted test-tube of water standing over water. A rapid action ensues and the test-tube is soon full of gas. The gas is very light and the test-tube must be kept with the open end downwards or the gas will instantly escape. If the tube of hydrogen be brought up to a flame, it catches fire with a sharp explosive click. The flame is practically invisible, so special care must be taken that nothing catches fire from it accidentally. In this action the sodium has displaced half the hydrogen from the water acted upon and remains in solution, combined with the oxygen and the rest of the hydrogen in the water; the resulting product found dissolved in the water is called "sodium hydroxide". The old name was "sodium hydrate", but "hydrate" is an ambiguous term, as it is sometimes used for a combination of a substance with water without any displacement. The term "hydrate" is best used only in this latter sense, and not applied to a hydroxide.

Powdered magnesium also decomposes water, the action being very slow in the cold. On boiling, the action is more rapid. Finely divided aluminium also liberates hydrogen from boiling water.

47. Some metals which do not act appreciably on cold water will decompose steam when hot enough (see § 604). If a piece of zinc is placed in a tube and heated in a current of steam, the zinc replaces the hydrogen and becomes converted into zinc oxide, hydrogen being liberated. Cadmium, magnesium and iron act in a similar way. In the case of iron the oxide produced is the magnetic oxide already referred to.

The so-called "noble" metals, gold, silver, platinum, and also copper, which in some ways resembles silver, will not decompose water.

If a piece of zinc is placed in a solution of copper sulphate it becomes coated with copper. A piece of zinc with copper on it is called a zinc-copper couple; it will decompose water slowly even when cold. The copper does not enter into the action but acts as a catalyst, the zinc displacing the hydrogen (see § 602).

48. Hydrogen is conveniently prepared by replacement of the hydrogen of an acid by a metal. There are several acids which can be used for the purpose and a fairly large number of metals. The most usual pair are commercial zinc and dilute sulphuric acid (see § 602). The acid must not be concentrated. A suitable concentration is obtained by adding one volume of acid to about seven volumes of water. Note that the acid is added to the water. This should be done gradually and with constant stirring, as a great deal of heat is produced on mixing. If the water is added to the acid, the rise in temperature is so rapid that it may break the vessel and also steam may be formed with almost explosive violence. The zinc should not be pure. Dilute sulphuric acid does not act on pure zinc, but the impurities, chiefly carbon, in ordinary commercial zinc act as a catalytic agent. If pure zinc is used, the action will take place if a drop or two of copper sulphate solution is added.

Iron and hydrochloric acid may similarly be used, or aluminium and hydrochloric acid.

Hydrogen is usually produced in this way in a Wolff's bottle,

i.e. a bottle with two necks, as shown (fig. 13). A delivery tube comes from one neck and the other carries a thistle funnel. The latter dips into the acid in the bottle, the former does not. Fresh acid can be added through the thistle funnel, and if by any chance the delivery tube becomes stopped up, the rise of pressure in the flask forces the acid up into the thistle funnel. A modification of this arrangement is Kipp's apparatus. Here

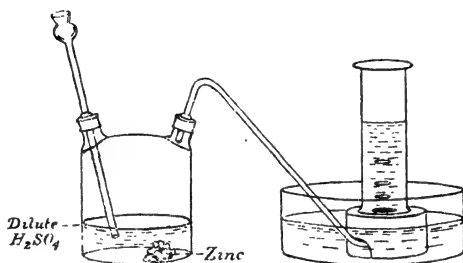


Fig. 18. Preparation of Hydrogen.

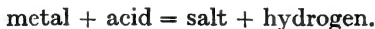
the funnel is enlarged to be as big as the bottle. The zinc is placed round the narrow waist at *W*. When no gas is being drawn off, the pressure drives the acid off the zinc and up into the top and the action stops. On opening the tap the pressure is relieved; the acid flows down and reaches the zinc. In this way gas is produced as long as it is being drawn off but stops as soon as no more is wanted (fig. 8).

49. It is as well here to turn attention away from the hydrogen for a moment and enquire what has happened to the zinc. Suppose zinc is added to the acid until no more will dissolve. At this stage it is clear that all the acid has been used up. The liquid is no longer sulphuric acid. It is something different and it contains some compound of zinc in solution. The liquid can be put into an evaporating dish and heated until most of the water has been driven off as steam. If the solution is then allowed to cool, it will be found that a white crystalline solid

appears in the liquid. This is the substance formed by the replacement of the hydrogen of the acid by the zinc. It is called "zinc sulphate" and is an example of a "salt". The action may be written:



This is a particular case of a common kind of action which may be written:



Not all acids, however, give free hydrogen when they act upon a metal. Sometimes there is secondary action where the hydrogen at the moment of its formation (i.e. when it is in the "nascent" state) attacks the acid present and quite different substances are produced. Nitric acid, for example, is not generally available as a source of hydrogen in this way. This will be clear after the properties of nitric acid have been studied.

50. Hydrogen is also produced by electrolysis. **Electrolysis** is the splitting up of a substance by an electric current. Pure water is difficult to split up in this way, but if a little sulphuric acid is added and the ends of the wires from an electric battery—or, with care, from a direct-current main—are dipped into the acidified water, oxygen and hydrogen are released, the hydrogen at the kathode (i.e. where the current leaves the solution) and the oxygen at the anode. The kathode and anode are usually of platinum which is unaffected by oxygen or acids. If copper is used for the anode, it is found that oxygen is not liberated but

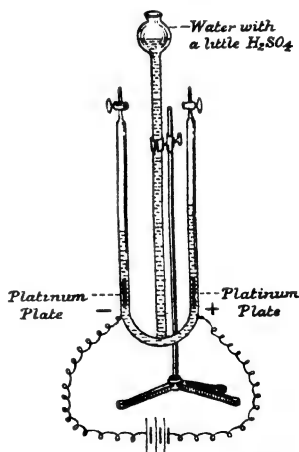


Fig. 14. Electrolysis of dilute Sulphuric Acid.

that the copper is dissolved. If a carbon rod is used for the anode, the gas evolved there consists mainly of a mixture of carbon monoxide and carbon dioxide. The usual apparatus for this purpose is called "Hoffman's Voltameter" and is shown in fig. 14. The gases collect in the vertical tubes and may be drawn off by opening the taps shown. The instrument is called a voltameter, or electricity measurer, because the amount of electricity passed through the apparatus may be calculated from the weight of gases liberated in a definite time.

Hydrogen is produced as a by-product in the manufacture of caustic soda, by electrolysis of common salt, and this is the source of a great deal of the hydrogen of commerce (see § 513).

51. Alkalis are a well-marked group of chemical compounds which contain hydrogen and some of them readily yield hydrogen with a metal (see § 611). For example, if zinc or aluminium is dissolved in a solution of sodium hydroxide, which is one of the most familiar of the alkalis, hydrogen is evolved.

52. Much hydrogen is produced by the "destructive distillation" of coal, i.e. by heating coal strongly without allowing any air to get to it. This is the way in which coal gas is made. As the gas contains 45 to 50 per cent. of hydrogen, this is an exception to the statement made earlier that hydrogen could not be made by heating a familiar substance. The hydrogen prepared thus, however, is only one ingredient of many in a complicated mixture, and it is not easy to obtain pure hydrogen from it.

53. If steam is passed over red-hot carbon, e.g. coke, the carbon replaces the hydrogen to produce an oxide of carbon—carbon monoxide—which mixes with the hydrogen; the product of the action is a mixture of hydrogen and carbon monoxide called *water gas*. The carbon monoxide as well as the hydrogen is an inflammable gas, and hence the mixture is useful as a gaseous fuel and can for some purposes replace coal gas. Notice how very cheap the raw materials are—coke and water.

54. An interesting reaction yielding hydrogen is that between

sodium hydroxide and sodium formate when heated together. The special point of this action will be realised later (see § 251).

55. Hydrogen is the lightest gas known, hence its use for filling airships and balloons. Its value for this purpose is much lowered by its being inflammable. This is especially a disadvantage in war. The rout of the Zeppelins in the Great War was largely due to the fact that they could so easily be set on fire. Consequently great efforts have been made to obtain at low cost the non-inflammable gas helium, which, although twice as dense as hydrogen, is much lighter than coal gas and will not burn under any circumstances.

56. Hydrogen is but very slightly soluble in water. It can only be liquefied with great difficulty, the boiling-point being -253°C . It has also been solidified at only a few degrees above the absolute zero. Hydrogen burns, but will not support combustion. If a lighted taper is passed up into a jar of hydrogen—held mouth downward, or all the gas will escape in a moment—the taper ignites the gas at the mouth, but is itself extinguished. It should be noted, however, that when one gas burns in another, it is only a matter of convenience which is said to burn in which. If a jet of air is ignited in an atmosphere of hydrogen, the air appears to burn just as in normal circumstances the hydrogen burns in air. This fact may easily be illustrated by the apparatus, consisting mainly of an oil-lamp chimney, shown in fig. 15. Coal gas can be used instead of hydrogen and is passed in at *A* and ignited at the top at *B*. Air passes in at *C*, being drawn through by the current of gas. If now a match is passed through the tube *CD* the air takes fire and burns at *D*.

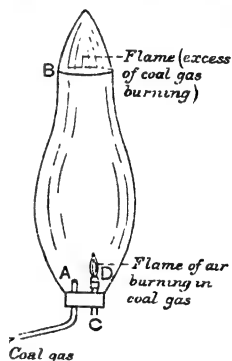


Fig. 15. Air burning in coal gas.

57. Hydrogen, having no colour, smell, or taste, might easily be overlooked when it is given off in a reaction. It is usually recognised by the way it burns—with a *very* light blue flame.

When hydrogen burns water is formed, though it takes a large amount of hydrogen to yield any appreciable quantity. If a cold surface is held in a flame of hydrogen or coal gas for a moment, it becomes covered with a film of condensed steam. The gases from burning coal gas or hydrogen may be led through a tube surrounded by a current of cold water and in this way an appreciable amount of water may be collected (see also § 603).

It should be noticed that water is the *only* product of its combustion. This helps to distinguish it from other combustible gases which yield products with well-marked properties (see §§ 679 and 680).

Chapter VI

THE MOLECULAR THEORY

58. We have seen (chap. III) that some properties of gases are common to all gases; for instance, they all obey Boyle's Law and Charles' Law. The study of physics brings to light other facts that are true of all gases, and speculation naturally arises as to what there may be about the nature of gases which makes them all behave similarly. We are entitled to make any guess we like and then see how far it fits the facts. Such a scientific guess is called a "hypothesis" before it is established and a "theory" if it agrees with the results of experiment and observation. In the past many such guesses have been made and most of them discarded because they did not fit in with experimental results. The modern student is fortunate in that he does not have to spend over much of his time investigating the hypotheses which have been proved to be wrong, and we will at once turn to those which have stood the test of experience. The reader may not be much impressed with the likelihood of the truth of these theories when first he meets them. Other views may seem equally plausible. We shall, however, state the accepted theories at the start, with an indication of the evidence for them. The student will be in a much better position to appreciate their truth at the end of the book, when we shall return to this question again. This is the true scientific order. First we have a number of well-investigated experimental facts, which need explaining. Then we have the hypothesis, then the test of it—and the majority of the facts and explanations throughout this book form the test—and then a re-examination of the theory in the light of this further experience.

59. *A gas, then, is supposed to consist of a large number of*

small particles, separate from each other, moving about very rapidly in a space. The speed of their movements is determined by the *temperature*. The *pressure* is due to their bombardment of the sides of the vessel. A rise in temperature quickens the speed and so increases the bombardment or pressure, unless the volume is allowed to increase. Boyle's Law can, in fact, be deduced mathematically from the known properties of moving bodies, if the constitution of a gas is as described. The particles of a gas are called "molecules", and a single molecule is supposed to be the **smallest particle of the substance in question which can exist alone and possess its distinctive properties.**

If we accept this idea of a gas, it will be an easy step to suppose that when gases act upon each other chemically it is really the *molecules* which act. If we examined a large number of cases where gases combine together, we should expect to find an example of the very simplest possible case, where one *molecule* of the first gas acts upon one of the second, and where consequently an equal number of molecules of the two gases interact. Now on investigating actions between two gases we find examples of the very simple case in which equal *volumes* of the gases take part in the action. Moreover, we also find that whenever gases act upon each other chemically the volumes taking part in the action and the volumes of any gases formed by the action are *all in a simple numerical ratio to one another*. Numerous examples of this will be met with. The following are a few of them which will be discussed fully in their appropriate places. The volumes are given in litres, but of course any definite volume will do provided the proportions remain the same. The volumes are supposed to be measured under the same conditions of temperature and pressure both before and after combination:

2 litres of hydrogen combine with 1 litre of oxygen to form 2 litres of steam.

1 litre of hydrogen combines with 1 litre of chlorine to form 2 litres of hydrochloric acid gas.

2 litres of carbon monoxide combine with 1 litre of oxygen to form 2 litres of carbon dioxide.

The essential thing to notice is that we *never* get such a case as :

1 litre of gas *A* combines with 1.516 litres of gas *B* to form 2.611 litres of gas *C*.

All the numbers in real cases are simple. This simple relation between combining volumes of gases and the resulting volumes is an enormous help.

The law is called **Gay-Lussac's* Law of Volumes**, and its discovery marked a very definite advance in chemistry. It may be stated in the following words: **The volumes of gases which react bear a simple relation to one another and to the volume of the product if that is gaseous** provided that the volumes are measured under the same conditions of temperature and pressure. Note that the law is an experimental fact and is true whatever theories we may form about the nature of gases or of chemical action. When, however, we put this law beside the mental picture we have formed of a gas and the view that chemical action takes place between the molecules of gases, we at once see that *there must be some simple relationship between the number of molecules in equal volumes of different gases*. As a first hypothesis, and considering the idea we started with that all gases have some properties in common, we suppose that

Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.

This is **Avogadro's Law**; it is one of the most important in the whole realm of chemistry. We shall be constantly applying it and always getting results which agree with experiment, and in this way our confidence in the law will be established.

On the molecular theory, the simplest case of two gases interacting occurs when one *molecule* of one gas combines with

* 1778-1850, Professor at the Sorbonne, Paris.

one *molecule* of another. Under Gay-Lussac's Law, the simplest case occurs when 1 *litre* of one gas combines with 1 *litre* of another. It is a very natural and obvious guess from this that the simplest case from the one point of view is identical with the simplest case in the second. This suggests Avogadro's Law at once.

60. The law enables a comparison to be made between the molecular weights of different gases, or of different compounds which can be examined in a gaseous state. We only require to know the weights of equal volumes of the two gases. Suppose, for example, the same volumes of two gases, *A* and *B*, weigh *x* gm. and *y* gm. respectively. We do not know how many molecules we are dealing with, but by Avogadro's Law it will be the same number, *n*, for both. We have then

$$\frac{\text{weight of } n \text{ molecules of } A}{\text{weight of } n \text{ molecules of } B} = \frac{x}{y}.$$

$$\therefore \frac{\text{weight of 1 molecule of } A}{\text{weight of 1 molecule of } B} = \frac{x}{y}.$$

We can, therefore, choose any standard gas, assign a number to represent its molecular weight, and then measure the molecular weights of other gases with this as a standard. It is a matter of arithmetical convenience which gas we choose as our standard. Hydrogen is the lightest gas known and hence was originally chosen as the standard. It would seem obvious to take the molecular weight of hydrogen as 1 and to measure the molecular weights of other gases as multiples of it. But this is not done. The reason will be seen if we consider the two following cases:

61. Two litres of hydrogen combine with 1 litre of oxygen to give 2 litres of steam. Suppose a litre of any gas contains *n* molecules. By Avogadro's Law *n* is the same for all gases. So 2*n* molecules of hydrogen and *n* molecules of oxygen give 2*n* molecules of steam. Hence to get 1 molecule of steam we require half a molecule of oxygen.

Again, 1 litre of hydrogen combines with 1 litre of chlorine to give 2 litres of hydrochloric acid gas. Reasoning as before,

1 molecule of hydrochloric acid contains half a molecule of hydrogen and half a molecule of chlorine. Hence the molecules of oxygen, hydrogen and chlorine are all capable of being halved. The two halves do not exist separately in the gas. This would be contrary to our conception of a molecule. The conclusion is that they are combined together. Obviously a molecule of a compound substance like steam is not simple. We conclude that the molecule of an elementary gas like oxygen, hydrogen or chlorine is not simple either. It must consist of two halves which on combination with another gas can enter into different molecules. There might seem to be no reason why a molecule of hydrogen could not be split up into four, six or more even number of parts. Why not, if it can be split up into two? We are, however, trying to build up an explanation of the things we find happen. It is a great help and makes the matter much clearer if we suppose each hydrogen molecule to contain *two* parts, which can, when a chemical action takes place, pass into two different molecules of the compounds formed. On the other hand it never helps the explanation to suppose that the hydrogen molecule contains more than two such parts, and a half molecule of hydrogen is found in practice to be the smallest weight we ever have to consider. The molecular weight of hydrogen is then taken to be 2, and other molecular weights are measured with this as the standard. The half-molecule of hydrogen is called an *atom* of hydrogen. This word "atom" will be explained more fully in chap. VIII.

62. Suppose D is the density of any gas compared with hydrogen as standard:

$$\begin{aligned}
 D &= \frac{\text{weight of any volume of the gas}}{\text{weight of same volume of hydrogen}} \\
 &= \frac{\text{weight of } n \text{ molecules of the gas}}{\text{weight of } n \text{ molecules of hydrogen}} \\
 &= \frac{\text{weight of 1 molecule of the gas}}{\text{weight of 1 molecule of hydrogen}} \\
 &= \frac{\text{molecular weight of the gas}}{2}.
 \end{aligned}$$

Hence the density of any gas compared with hydrogen is half the molecular weight. This useful fact should be carefully noted. It provides the readiest and simplest method of finding the molecular weights of many substances. In the next chapter its usefulness is extended to vapours of substances which are not gases at ordinary temperatures.

63. One further point. The molecular weight of oxygen turns out to be, on the above scale, a trifle under 32. Now oxygen is made more use of in practical work than hydrogen; it forms more compounds and those more convenient for study. Hydrogen, too, is very light, and it is preferable when weighing substances to have as large a weight as possible to deal with, as, the total error being well defined, the percentage error is smaller on a large weight than on a small one. For these reasons it has now been decided that it is preferable to take oxygen as the standard and to call its molecular weight 32.

On this scale the other molecular weights are a trifle higher, that of hydrogen being slightly over 2, or more accurately 2.016. Until somewhat advanced work is undertaken the difference between these two scales can be ignored.

Chapter VII

THE MOLECULAR THEORY (SOME CALCULATIONS)

64. In the preceding chapter it was seen that provided the weight of a volume of a gas at standard temperature and pressure (i.e. 0°C . and 760 mm. of mercury) can be found, its molecular weight can be found. Or, further, if the weight of any volume of the gas at any measured temperature and pressure is known, the molecular weight can be found, for by Charles' Law and Boyle's Law the volume it would occupy at the standard temperature and pressure can be calculated. The phrase "standard temperature and pressure" is often written in short as "S.T.P." or sometimes as "N.T.P.", i.e. "normal temperature and pressure".

65. By very careful experiment it has been found that 2 gm. of hydrogen occupy 22.4 litres at S.T.P., 2 being, as already explained, the molecular weight of hydrogen. Suppose, now, we consider another gas, which we will call X , whose molecules are, say, each five times as heavy as a hydrogen molecule, i.e. its molecular weight is 10. Suppose we take two vessels, each with a volume of 22.4 litres, and fill one with hydrogen and the other with the gas X , both at S.T.P. The gas in the former weighs 2 gm. Now by Avogadro's Law the second space contains exactly as many molecules as the first; but each is five times as heavy, i.e. the whole weighs 10 gm. Hence 22.4 litres of a gas of molecular weight 10 weigh 10 gm. This is a simple case. It can easily be seen in this way that **the molecular weight in grammes of any gas occupies 22.4 litres at S.T.P.** This is a most important result and must be carefully noted and committed to memory. It will be needed frequently, and many problems will be met with which involve its use.

It will be readily seen that it gives a simple way of regarding the problem of finding the molecular weight of a gas. "What is the molecular weight of this gas?" may be re-worded "What is the weight in grams of 22.4 litres of this gas measured at s.t.p.?" If therefore a known volume of the gas can be weighed under known conditions of temperature and pressure, the molecular weight can be calculated. There is an important and exceedingly useful extension of this. If a substance is not a gas at s.t.p. it can sometimes be turned into a gas by being heated above its boiling-point. There is no need to consider the details of the experiment for the moment. The interesting and important thing to notice is this: Although the substance is not a gas at s.t.p., yet if the weight, volume and pressure are observed at a temperature above the boiling-point and a calculation is made by means of Boyle's and Charles' Laws of the volume which the vapour would have occupied at s.t.p. if it could have remained gaseous, then the weight of 22.4 litres calculated in this way still gives the molecular weight in grammes.

For example, suppose that it is found by any method that at 760 mm. pressure and a temperature of 136.5°C . 11.2 litres of steam weigh 6 gm., 136.5°C . is 409.5°A.T.

Since the volume is proportional to the absolute temperature, this same steam, if it remained a gas, would occupy at 0°C . (i.e. 273°A.T.)

$$\frac{11.2 \times 273}{409.5} \text{ litres or } 7.47 \text{ litres.}$$

Hence 7.47 litres weigh 6 gm., or 22.4 litres would weigh

$$\frac{6 \times 22.4}{7.47} = 18 \text{ gm.}$$

Hence 18 is the molecular weight of steam.

In practice it is quite common to find by calculations of this sort the imaginary weight of a substance considered as a gas at temperatures or pressures where it does not really exist as a gas.

If the reader feels that this is not quite fair—as he may quite reasonably do—the difficulty can be got over in this way:

66. What we are aiming at is comparing the weight of the gas with the weight of an equal volume of hydrogen by making use of the known fact that 2 gm. of hydrogen occupy 22.4 litres. Since, then, the steam cannot be cooled down to 0° C. and remain steam to be compared with the hydrogen, there can, at any rate, be no objection to heating up the hydrogen to the temperature of the steam.

So the same problem can be solved thus:

2 gm. of hydrogen at 273° A.T. occupy 22.4 litres.

∴ 2 gm. of hydrogen at 409.5° A.T. occupy

$$\frac{22.4 \times 409.5}{273} = 33.6 \text{ litres.}$$

∴ 11.2 litres of hydrogen at 409.5° A.T. weigh

$$\frac{2 \times 11.2}{33.6} = 0.667 \text{ gm.}$$

But 11.2 litres of steam at 409.5° A.T. weigh 6 gm. The steam and the hydrogen, having the same volume, under the same conditions of temperature and pressure, contain each the same number of molecules. Hence the ratio of the weight of 1 molecule of steam to that of 1 molecule of hydrogen is $\frac{6}{0.667} = 9$. So, finally, since the weight of a molecule of hydrogen is to be taken as 2, that of a molecule of steam is 18 as before. We have thus arrived at the same result, without assuming anything impossible about the properties of steam and water.

The second method may be a little more convincing; the first is perhaps somewhat simpler in actual use.

67. The point we have arrived at is this: The molecular weight of a gas can be determined by weighing a known volume of it; also the molecular weight of the vapour of a liquid or solid can be determined by finding the density of the vapour.

This requires that the vapour shall not be decomposed by heat. In this way the molecular weights of the ordinary gases have been determined and also of the vapours of many liquids and some solids. But the method is not applicable to most of the compounds of the metals, which are only vaporised at high temperatures—too high for the experimental determination of the density then to be possible. Thus, although the molecular weights of water, alcohol and ether can be determined without difficulty as they are easily volatile, a substance like the common oxide of iron would require far too high a temperature to convert it into a vapour for the determination to be practicable. Nor is it applicable to a substance like sugar which is decomposed chemically on heating.

Later on the reader will meet with other methods of finding molecular weights which can be used for many of the cases where the vapour density method is not practicable.

68. There is a point which should be noticed here. We say the molecular weight of steam is 18. Eighteen what? The answer is, eighteen times the weight of a half-molecule, or "atom", of hydrogen. What that weight, as a minute fraction of a gramme, may be, is of no importance for our present purpose. The weight of the hydrogen atom is the unit in which weights of atoms and of molecules are measured. It serves its purpose well, namely to enable us to compare one molecular or atomic weight with another.

Chapter VIII

ATOMS, ATOMIC WEIGHTS AND FORMULAE

69. We have seen in § 61 that the molecules of elementary gases like hydrogen, oxygen and chlorine consist of two halves, which, when a chemical action takes place, can separate and enter into different molecules of the compound or compounds produced. This leads us to the idea of something smaller than the molecule, namely the atom.

An atom is defined as *the smallest particle of an element which can take part in any chemical action or which can exist in a molecule of any compound*. The atoms are the interchangeable “spare parts” of chemistry. All atoms of the same element are regarded as indistinguishable, and so are all molecules of the same substance.

70. We are assuming, then, that the molecules of a substance—solid, liquid or gas—are built up of atoms. Each molecule of the same substance will contain the same number of atoms of the same elements arranged together in the same way. This fits in well with the **Law of Definite Proportions** to which reference was made in chap. I, § 9, which we will state again in more precise terms: *Each chemical compound however it is made always contains the same elements in the same proportions by weight*.

71. If chemical combination takes place between atoms, there is no obvious reason why the atoms of, say, two elements should always be combined in the same proportions and form the same compound. There might be one compound of two elements *A* and *B* in which the atoms were in the proportion of one of *A* to one of *B* and *another compound* of the same elements in which the atoms were in the proportions of one of *A* to two of *B*. There are many examples of two (or more) compounds of the same

elements. Investigation of some of them led Dalton to enunciate the second law of chemical combination, or the **Law of Multiple Proportions**, which may be stated in the form:

If two elements A and B combine together to form more than one compound, the weights of B which combine with unit weight of A in the different compounds are in the ratio of simple whole numbers.

Very many examples might be given in support of this law; a few historical ones will suffice.

		Weights of		Ratios of weights of oxygen
		Metal	Oxygen	
Lead:	brown oxide	1	0.154	2 to 1
	yellow oxide	1	0.0772	
Copper:	black oxide	1	0.252	2 to 1
	red oxide	1	0.126	
Iron:	ferric oxide	1	0.43	3 to 2
	ferrous oxide	1	0.287	
		Sulphur		
Sulphur:	sulphur trioxide	1	1.5	3 to 2
	sulphur dioxide	1	1.0	
		Carbon		
Carbon:	carbon dioxide	1	2.66	2 to 1
	carbon monoxide	1	1.33	

72. There is a third law of chemical combination which can easily be interpreted by the Atomic Theory. It is the **Law of Reciprocal Proportions**, which states that:

The relative proportions in which two elements combine with a third element are in simple ratio to those in which they combine with a fourth element or with one another.

To take a simple example, the ratio of the weights of chlorine and oxygen which combine with 1 gm. of lead in the chloride and oxide respectively is the same as the ratio of the weights of chlorine and oxygen which combine with 1 gm. of copper and is the same as the ratio in which chlorine and oxygen are combined together in chlorine monoxide.

Thus

1 gm. of lead combines with 0.342 gm. of chlorine in the chloride and 0.0772 gm. of oxygen in the oxide: ratio

$$\frac{\text{chlorine}}{\text{oxygen}} = \frac{4.43}{1}.$$

1 gm. of copper combines with 1.115 gm. of chlorine in the chloride and 0.252 gm. of oxygen in the oxide: ratio

$$\frac{\text{chlorine}}{\text{oxygen}} = \frac{4.43}{1}.$$

The ratio of $\frac{\text{chlorine}}{\text{oxygen}}$ in chlorine monoxide = $\frac{4.43}{1}$.

73. The preceding chapter left us in a position to find out by experiment the molecular weights of a number of common substances, compounds of elements which are not metals. Compounds of metals usually, though by no means always, have too high a boiling-point for the vapour density to be determined. Let us fix our attention for a little while on the non-metals and their compounds.

It is frequently possible to find out by direct experiment what elements a compound is made up of and in what proportions. To do this it is not necessary to have any very special ideas as to the nature of compounds or of chemical action. A good many cases will be found throughout this book of substances which can be accurately **analysed**, i.e. split up into the elements they contain, or **synthesised**, i.e. built up from the elements they are made of. We shall quote some of these results now, borrowing the information from other chapters. It is especially important to notice here that the results we are borrowing do not depend on any particular theory. If they depended upon the theory we are trying to build up we should be "arguing in a circle". This is a common kind of bad reasoning which it is most important to avoid. It is more necessary to be able to avoid arguing in a circle than it is to know something about chemistry. If we set

out to prove a thing it is most essential that the facts on which the proof is based do not take for granted the thing we are trying to prove. A large number of the bad arguments in the world are bad because they do this.

74. With this caution we can anticipate results and construct the following table, using the term "gramme-molecule" in its usual sense of the number of grammes of a substance equal to the molecular weight.

	Molecular weight	Grammes of oxygen in the gramme-molecule
Oxygen	32	32
Carbon monoxide	28	16
Carbon dioxide	44	32
Steam	18	16
Nitrous oxide	44	16
Nitric oxide	30	16
Sulphur dioxide	64	32
Alcohol	46	16

A table of this kind can be made for a large number of compounds containing oxygen, and it is found that the number in the second column is always 16 or a simple multiple of 16. Using, in the regular way, the weight of an atom of hydrogen as the unit, a molecule of steam weighs 18 of these units and the oxygen it contains weighs 16. Now does the molecule of steam contain one atom of oxygen, or two or three—or how many? Since no compound in the list contains less than 16 of oxygen, it is natural to suggest that, this being the least, we are here dealing with a case in which the molecule contains one atom of oxygen only. This is supported by the fact that the next higher on the list contains 32, i.e. twice 16, and suggests two atoms of oxygen to the molecule. If the list were to be extended, cases could be found where the weight of oxygen is 48 or 64, always multiples of 16. Clearly the atom of oxygen cannot weigh more than 16, as otherwise five compounds in the short list above would contain less than one atom of oxygen per molecule each. This, of course, would be contrary to the whole idea of the atom. But might

they not contain, say, each two atoms of oxygen, the atom of oxygen weighing 8? That would not be impossible. But if the atomic weight were 8 there would be no compound of oxygen known to contain only one, or indeed any odd number of atoms. There is no need to assume any smaller weight than 16 for the atomic weight of oxygen. 16, then, let it be.

75. A similar table can be made out for compounds of other elements. For example for carbon we have:

	Molecular weight	Grammes of carbon in the gramme-molecule
Carbon monoxide	28	12
Carbon dioxide	44	12
Marsh gas	16	12
Acetylene	26	24
Benzene	78	72
Carbon disulphide	76	12
Alcohol	46	24
Ethylene	28	24
Propylene	42	36
Ether	74	48

The reader should have little doubt from the above that the atomic weight of carbon is 12. In these cases it is important to note that the large number of chemical compounds which have been examined have never required chemists to assume numbers other than 16 and 12 for the atomic weights of oxygen and of carbon respectively. Lists such as the two given make the atomic weights stated very likely, and the continual testing of these results by using them in all kinds of chemical discussion and finding they give good results is the really final reason for their acceptance.

76. To determine the atomic weight of an element by this method it is necessary:

(1) To find the molecular weights of a large number—the larger the better—of compounds of the element. This can be done by selecting compounds whose vapour densities can be found and then applying the results of Avogadro's Law.

(2) To find by any means available the percentage composition (by weight) of the same compounds. Knowing from (1) the molecular weight, a table can then be drawn up like those already given for oxygen and carbon, showing the weight of the element which occurs in the gramme-molecule of each of the compounds considered. **The least of these weights is the required atomic weight** and the others will be simple multiples of it.

In this way the atomic weights of the commoner non-metals can be determined. A few results which can be thus obtained are as follows:

Hydrogen	1	Sulphur	32
Carbon	12	Chlorine	35.5
Nitrogen	14	Bromine	80
Oxygen	16	Iodine	127

77. The atomic and molecular theory leads to a simple and remarkably helpful way of writing some of our chemical knowledge in an abbreviated form. Each element is given a *symbol* of one or two letters which stands for one atom of that element. If, then, a molecule consists of a number of atoms chemically combined, the molecule may be indicated by writing down the symbols for the atoms it contains. Thus, if a substance is found to consist of molecules each made up of an atom of sulphur combined with two atoms of hydrogen, it may be written HHS, or more briefly H_2S . Water consists of molecules made up of two atoms of hydrogen and one of oxygen and so is written H_2O .

The presence of *formulae* of this sort on almost every page of a chemistry book gives the work an air of mystery to the uninitiated. But in reality far from complicating the subject these formulae very much simplify it, and for this reason we have introduced the reader to them as early as possible. What, to take a parallel case, would algebra be like, if instead of writing

x^2 one had to write " x squared" every time, or to write " a multiplied by b " instead of ab ? Imagine the labour of trying to solve a quadratic equation with such limitations. The reader is making chemistry much easier for himself by getting used to these formulae, as he quickly will.

78. So far the student has been shown how to find the atomic weights of some only of the elements. We will return to the question of formulae when he has seen how to determine more atomic weights, including those of the more familiar metals. He should find it more satisfactory to work with atomic weights and formulae after he has discovered how they are ascertained.

It should be noted that there are quite a number of compounds of metals of which the vapour densities can be found. But there are many more of which they cannot. And to determine an atomic weight, a list of molecular weights of a few compounds of an element is not sufficient. We require a great many of the same element before the atomic weight can be decided with any certainty. A method for the determination of the molecular weights which does not depend directly upon vapour densities and Avogadro's Law will be explained later (§ 433).

Chapter IX

WATER

79. The ancients recognised four elements, earth, fire, water and air, and the word "element" is still sometimes used in this way in a non-technical sense. We now know that "earth" is not by any means an exact term; many hundreds of totally different substances are included under the term "earth". "Fire" is not a substance at all; almost any material may become hot and luminous if it is undergoing a brisk chemical change, and so for the time being may be termed "fire". Nor is the term "element" appropriate for water or air; water is a compound; air is a mixture.

Water and air are two of the most important substances in our daily lives. We shall study them for their own sakes. The student will also do well to contrast them, as this will help him to get thoroughly fixed in his mind the differences between a mixture and a compound.

80. To establish the composition of a substance, we may proceed either by **analysis**, i.e. by splitting the substance up to see what it yields, or by **synthesis**,* i.e. by building up the substance from its constituents and deducing its composition by considering what was put into it. In the case of substances which are gases or are easily evaporated, the composition may be determined either by *weight* or by *volume*. The relative densities of the gases involved being known, these two methods do not give us different information, as we can calculate the weights from the volumes and *vice versa*. Either may be used to confirm the other.

* "Synthesis" in Greek means "putting together".

In the problem of finding by experiment the composition of water, then, we have four different ways of proceeding:

- (1) Analysis by volume;
- (2) Synthesis by volume;
- (3) Analysis by weight;
- (4) Synthesis by weight.

81. Method (1), analysis by volume. This is done by electrolysis. The process has been described in chap. v (*q.v.*)* The method has two sources of error. In the first place oxygen is slightly more soluble in water than is hydrogen. In the second, some of the oxygen is converted into ozone, a form of oxygen which is denser than ordinary oxygen (see § 485) and which consequently occupies less volume. Both these errors are small; they both tend to make the volume of oxygen as measured a little less than it should be.

82. Method (2), synthesis by volume. A graduated thick glass tube, like a barometer tube, full of mercury, is inverted in a bowl of mercury. Two short platinum wires pass through the tube with their ends close together (see fig. 16). Such a tube is called a "eudiometer tube". Into this tube a quantity of dry oxygen is passed. The tube is lowered until the mercury inside is on a level with the mercury outside. This ensures the pressure inside being the same as the atmospheric pressure outside. The volume of oxygen is now read. Then some dry hydrogen is introduced and the total volume read after levelling as before, the difference between

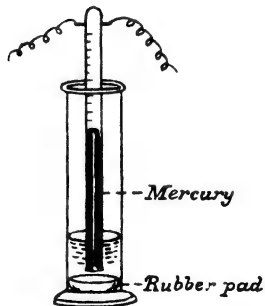


Fig. 16. Combination of Hydrogen and Oxygen.

* If it be objected that we are here dealing not with water but with dilute sulphuric acid, it may be noted that it can be shown that there is just as much sulphuric acid left after the action as before it, whereas the amount of water present has diminished. Hence the hydrogen and oxygen produced

the two readings giving the volume of hydrogen. The open end of the tube is now pressed down on to a pad of india-rubber and an electric spark passed between the platinum wires. There is a sharp explosion, the shock of which is absorbed by the rubber pad, and the volume decreases. If the volume of hydrogen used is just twice the volume of oxygen, there will be no gas left, but in this case the sudden rise of the mercury and its impact against the glass will probably break the tube. Hence it must be arranged that there will be some gas unchanged which must be measured; it will prove to be either all oxygen or all hydrogen. This volume, after levelling as before, is subtracted from the volume of that particular gas introduced and it is found that the volume of hydrogen used up is twice the volume of oxygen. The volume of water formed is very small indeed and can be neglected.

By introducing two volumes of hydrogen and one of oxygen into the eudiometer tube and keeping the whole at a temperature over 100°C ., the volume of water formed may be measured in the form of steam. To keep the water formed at such a temperature the tube is surrounded by a wider tube or jacket through which is passed the vapour of a liquid with a boiling-point appreciably



Fig. 17.

have been generated at the expense of a certain amount of water and of nothing else.

If sodium fluoride—a compound of sodium and fluorine—be dissolved in the water instead of adding dilute acid, oxygen and hydrogen are evolved on electrolysis just as they were from the dilute acid. In this case they clearly must have come from the water.

higher than that of water. Amyl alcohol, $C_5H_{11}OH$ (boiling-point $138^\circ C.$), is commonly used for the purpose. Fig. 17 shows a modified form of the apparatus which is more suitable when the water produced by the explosion is to be kept in the form of steam. The mercury is adjusted to the same level in both sides of the U-tube before any reading of the volume is taken. The open end is closed with the thumb during the explosion.

The volume of steam is always found to be the same as that of the hydrogen used. There are thus, by Avogadro's Law, as many molecules of hydrogen used as there are of steam formed. This agrees with the formula H_2O , for if this formula is correct two molecules of water would be formed from two molecules of hydrogen and one of oxygen. That is, two molecules of steam, each represented by H_2O , would be formed from two molecules of hydrogen, each represented by H_2 and one of oxygen, O_2 . Avogadro's Law practically comes to saying that a molecule of any gas occupies the same space as a molecule of any other. Hence it is clear that the above agrees with the fact that *steam is made up of its own volume of hydrogen and half its own volume of oxygen*—all, be it noted, measured at the same temperature and pressure.

The formula of steam, then, is H_2O . But we have not proved that this is the formula of water. The molecule of water may be, and probably is, a multiple of this. However, for all ordinary purposes the formula for water is taken as H_2O .

83. Method (3), analysis by weight. This can be done but does not prove a very good method in practice and so we pass on to

84. Method (4), synthesis by weight. This is the most accurate of the four methods. The experiment, a very important one, has been performed several times with very great care. Its special importance will be realised after reading chap. XI.

Dry, pure hydrogen is passed over red-hot copper oxide when an action takes place thus:



The copper oxide is weighed before and after the experiment, and the water formed is weighed also.

A number of chemical substances have a considerable "affinity" for water, that is, they readily combine with it. Such substances are sodium hydroxide or caustic soda, caustic potash, calcium chloride, concentrated sulphuric acid, and, one of the most striking examples, phosphorus pentoxide.

The hydrogen, then, is dried by passing it through tubes containing phosphorus pentoxide before reaching the copper oxide.

The apparatus is shown in fig. 18. The hydrogen is generated from zinc and dilute sulphuric acid and is passed through the first series of tubes. Of these the first contains caustic potash and the others phosphorus pentoxide. The last tube is weighed at

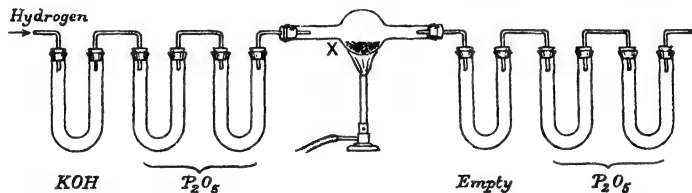


Fig. 18. Composition of Water.

the start and again after hydrogen has been passing through the tube for some time. This weight should be constant, showing that all the moisture in the hydrogen has been absorbed in the previous tubes and hence that the hydrogen is coming through dry. The phosphorus pentoxide is very efficient in absorbing water; the caustic potash retains other impurities in addition to water, which may possibly be found in the hydrogen. The hydrogen may be bubbled through lead nitrate solution as an extra precaution before being passed over the phosphorus pentoxide.

The hard-glass tube *X* contains black copper oxide which must be dried before use; it is weighed before and after the

experiment. The tubes on the right, which also contain phosphorus pentoxide, except the first which is empty and is cooled by being placed in water, are weighed before and after the experiment. Before the experiment is stopped the whole length of the tube is heated to make sure that no water has condensed in it, and the passage of the hydrogen is continued a little while after the heating has ceased. It is important that all the water produced should be passed over and absorbed and weighed in the tubes on the right.

It must not be forgotten that *there is always moisture in the air* and hence calcium chloride or phosphorus pentoxide exposed to the air will gain in weight. So when U-tubes containing such substances are weighed the ends should be closed with rubber tubes and clips to secure accuracy.

The calculation of the results is simple. The *decrease* in the weight of the tube *X* gives the weight of oxygen used, the *increase* of the tubes on the right the weight of water formed. The difference is the weight of hydrogen.

This is the method used by **Dumas*** in a classical series of experiments. He, however, used a spirit-lamp and not a bunsen burner.

By weight the amount of oxygen in the water is thus found to be slightly less than eight times the amount of hydrogen. For practical purposes it may be taken as eight.

85. A more direct and more exact synthesis of water was carried out by E. W. Morley in 1895.

Morley's apparatus is shown in fig. 19. The apparatus was evacuated and weighed; it was then filled with dry oxygen through one of the tubes *B, B*. Dry hydrogen was admitted through the other tube and ignited at the jet *A* by an electric

* Jean Baptiste Dumas (1800-84), one of the most famous of French chemists, was professor at the Sorbonne in Paris. Besides his research on the composition of water he is especially remembered by his work on the densities of vapours.

spark passed between the wires *F, F*. The hydrogen continued to burn in the oxygen so long as the supplies of the gases were maintained. The upper part of the tube *CD* was cooled with water and the lower part in a freezing mixture. Thus the water produced by the combustion was solidified into ice at *D*. The oxygen was delivered from two large globes which were carefully weighed before and after the experiment. But this method was not adopted for the hydrogen. It is difficult to weigh hydrogen accurately in large globes, as the gas is so very light that its weight is only a small fraction of the weight of the globes and consequently small errors in weighing the globes involve somewhat large percentage errors in the weight of the hydrogen. In order to avoid this difficulty Morley absorbed his hydrogen in the metal palladium. When this metal is heated to redness and allowed to cool in an atmosphere of hydrogen, large quantities of the gas are absorbed which are liberated again by heating the metal. In one of Morley's experiments 600 gm. of palladium (occupying about 53 c.c.) absorbed 3.8 gm. of hydrogen whose volume would be about 42 litres at S.T.P.

The apparatus was weighed before and after the experiment, being evacuated of gas on both occasions. The increase of weight gave the amount of water found. *B, B* were packed with phosphorus pentoxide, which retained any water that might have passed out at *B* during the evacuation.

Finally—no precaution being overlooked—the unused gas pumped out of the apparatus after the experiment was carefully analysed. The weight of any hydrogen found was subtracted from the weight of hydrogen given off from the palladium. Similarly any oxygen left over was allowed for.

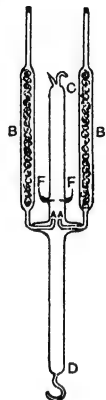


Fig. 19. Morley's Synthesis of Water.

In this way Morley obtained the figure for the composition of water:

oxygen to hydrogen 7.9396 to 1 by weight.

This was the mean of 12 experiments during which no less than 400 gm. of water were produced.

86. The enormous importance of water to man and to other living things, both animals and plants, is too obvious to need emphasising. It must not, however, be regarded as a happy accident that water, which is so essential, is also so plentiful. It is just because water is so plentiful that life has been able to develop on the earth. If water were rare, either life could never have appeared or else it would have appeared in quite a different form determined by some other common substance. It is also worth noting that life could not have developed if the temperature of at any rate part of the earth had not been such that water existed in the liquid state.

So also water has no taste or smell. Man's senses have developed with water always present, and consequently this serves him with a "base line" with which to compare other tastes and smells. As a matter of fact, *pure* water has a flat and insipid taste. But pure water is not a familiar substance in nature. The various natural waters contain solids or gases in solution. They all contain some dissolved air. Tap water contains a small quantity of common salt and frequently some carbonates in solution which determine whether the water is "hard" or "soft" (see chap. XVIII). Rain water is the purest of natural waters. Sea water, on the other hand, contains a great variety of dissolved salts of which common salt or sodium chloride is the most plentiful, about $2\frac{1}{2}$ per cent. There are also other metallic salts—sulphates, carbonates, and bromides—present, the metals being magnesium, calcium, potassium, with traces of other substances such as iron, silica, etc. River water is much purer than sea water, the actual composition depending largely on the nature of the soil through which it passes. Solid

matter obtained by evaporating river water is, however, usually very different from that obtained from sea water, being much richer as a rule in calcium carbonate, in sulphates and in silica.

Pure water may be obtained by boiling tap water and condensing the steam which comes off by passing it through a jacket of colder water. This may be conveniently done by Liebig's Condenser, which will be readily understood from fig. 20.

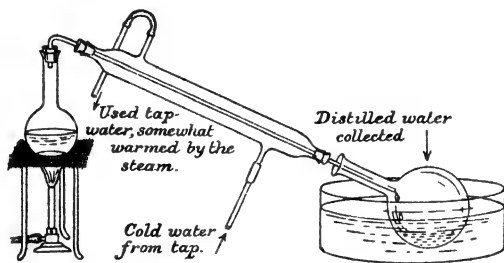


Fig. 20. Purification of Water by distillation.

87. There are no very obvious chemical tests for the presence of water. A small quantity of water may be recognised by its effect upon dry copper sulphate. This salt is familiar in the laboratory as large blue crystals. When thoroughly dried the substance turns white. Water restores the blue colour (see § 538).

Water can however be identified by its physical properties—its freezing-point $0^{\circ}\text{C}.$, its boiling-point $100^{\circ}\text{C}.$, and its density 1 gm. per c.c. at $4^{\circ}\text{C}.$ If these properties are to be used for identification, the water must be pure.

88. Three common terms should be noted here. They are used to describe the way in which a substance acts with regard to water vapour.

(a) Some substances absorb water vapour from any moist atmosphere. Some of them, usually salts, can absorb water from the atmosphere to such an extent that the whole of the solid is

dissolved. Such substances are called *deliquescent*. Examples are calcium chloride, caustic soda, caustic potash, and cobalt nitrate.

(b) Other substances absorb water vapour from the atmosphere but not to such an extent that they are dissolved. They are called *hygroscopic*. Examples are quicklime and anhydrous copper sulphate.

(c) Some substances which contain water of crystallisation (see chap. x, § 92) lose the whole or part of it when they are exposed to the atmosphere. They are called *efflorescent* substances. Washing soda is a good example. The clear crystals have the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; on exposure to the atmosphere they lose nine-tenths of their water of crystallisation and form a white powder, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

Chapter X

SOLUTION

89. When a piece of solid sugar is put into a glass of water it dissolves. It ceases to be a solid. It becomes liquid and mixes with the water in such a way that the resulting mixture is the same throughout, or, to use the scientific term, it is "homogeneous". We are so used to seeing things like this happen that we are apt to cease to wonder at them. Yet to a really scientific mind there is as much to reflect upon here as there is in science's more elaborate marvels such as X-rays or wireless. The difference between solid, liquid and gas (see chap. I) is really dependent upon the way the particles of a substance—the molecules—hold together. The force which keeps the particles of a solid together is called "cohesion". There is a little cohesion in a liquid, but not much. When a solid dissolves in a liquid the cohesion of the solid is for the most part destroyed. The solid becomes a liquid and forms an intimate mixture with the substance dissolving it, the **solvent** as it is called. The substance dissolved may be called the **solute** and the resultant mixed liquid the **solution**.

A piece of zinc can be dissolved in sulphuric acid, and in such a case there is a definite chemical action, new substances being formed. We are not now considering such cases. But even ordinary cases of solution do to a certain extent resemble chemical action. There is frequently a change in temperature, though this is often a fall, whereas in a chemical action which takes place without the application of heat we get a rise of temperature. A simple case of solution, however, differs from a true chemical action in two respects. There is no fixed relationship between the quantities, and the solvent and solute can easily be separated, usually by boiling the solvent away.

90. When a liquid is required pure, freed from any solid it contains in solution, it is *distilled*, i.e. the liquid is boiled and the vapour given off is condensed again into a liquid. This is conveniently done in such an apparatus as Liebig's Condenser, mentioned in § 86 and shown in fig. 20. For use on a larger scale the vapour is passed through a spiral tube, often called a "worm", immersed in a vessel of cold running water. In such a way distilled water is produced from tap water.

91. When a solid is dissolved in water it is found that a fixed quantity of the solvent will not dissolve more than a certain quantity of the solute. When this stage is reached the solution is said to be **saturated**.

The solubility of a solid in a liquid at any temperature may conveniently be defined by stating how many grammes of the solid dissolve in 100 gm. of the solvent at that temperature to form a saturated solution.

In most cases the *solubility of a solid increases as the temperature rises, but the rate at which the solubility rises varies very much for different substances*. Taking water as the solvent, ordinary salt is only a little more soluble at boiling-point than at ordinary temperatures, whereas at 0° C. potassium nitrate (saltpetre) is only about one-third as soluble as common salt, but at 100° C. it is more than six times as soluble. The effect of temperature on the solubility of a substance is conveniently shown on a graph such as that in fig. 21. Along the vertical axis is plotted the maximum amount of a substance which will dissolve in 100 gm. of water, and along the horizontal axis the temperature.

For the most part the curves show a regular rise in solubility with rise of temperature. Where the curve does not show a regular rise it can be explained by showing that at the temperature where the irregularity occurs there is a chemical change in the solute. A few substances are less soluble in hot water than in cold. Calcium citrate, calcium sulphate and calcium hydroxide are examples of this. Such cases, however, are rare.

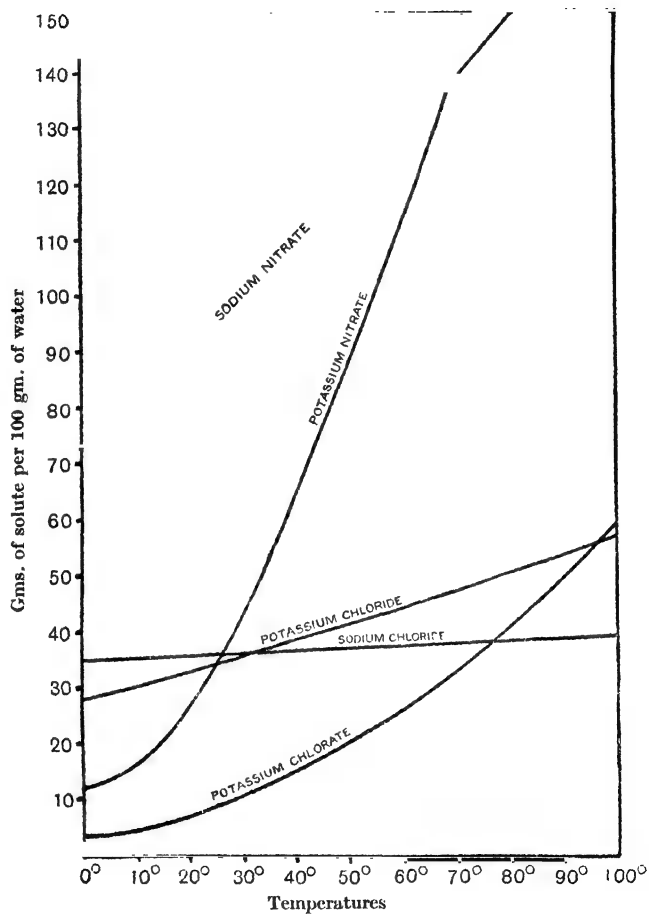


Fig. 21.

92. If a hot saturated solution be allowed to cool, the solution contains more of the solid than it can hold at the lower temperature and the excess is deposited. The deposit is frequently crystalline, i.e. it consists of small pieces of the solid of a definite geometrical shape and bounded by flat surfaces. These crystals, especially in the case of a salt, frequently contain water **chemically combined in a perfectly definite proportion with the salt**; the water so combined is called **water of crystallisation**. This water is generally loosely held and can in most cases be driven off by heating (but see § 197).

It is a fact worth noting that a molecule of a substance in such a case nearly always contains a whole number of molecules of water to one molecule of the salt. Thus we have $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue vitriol), $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (washing soda), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salts), etc. Cadmium sulphate, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, is curious as an exception. A salt can often be obtained in crystals of different kinds, having different amounts of water of crystallisation. For example, magnesium sulphate forms at least three "hydrates" (see § 46), $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. As the *anhydrous* salt (i.e. the salt with no water of crystallisation) and each of the hydrates has its own solubility, we see that such a phrase as "the solubility of magnesium sulphate" is not a definite one. The precise kind of sulphate must be specified.

93. It sometimes happens that when a hot saturated solution of a salt is cooled, there is no immediate deposit of the solute, although at the lower temperature the salt is less soluble, and so the solution contains more of the solute than a saturated solution would contain at the temperature. Such a solution is said to be **supersaturated**. It is unstable and may easily be made to deposit the excess. This may often be done by shaking or by dropping in a small particle of solid matter. A certain way is to drop in a particle, however small, of the solid salt. The result is an immediate precipitation of the excess, and the strength of the solution drops to the normal saturation strength

for the temperature. The distinction between the three types of solution—unsaturated, saturated and supersaturated—is easily seen by introducing a tiny piece of the solid in this way. If the solution is unsaturated the piece dissolves, if saturated nothing happens, if supersaturated a deposition of salt takes place from the solution.

94. Crystallisation is used as a method of separating salts from a mixture of salts all of which are soluble. Suppose the mixture is dissolved in water and the water is evaporated off by heating. It is clear that the least soluble ingredient will tend to crystallise out first, and if the difference in solubility is considerable, the bulk of one salt is obtained as crystals before any appreciable quantity of the other more soluble salts is deposited. The first crop of crystals can then be dissolved in water and crystallised afresh. This re-crystallisation yields a much purer specimen of the salt. The process can, if necessary, be repeated several times, the salt obtained being progressively purer at each stage. For example, potassium chlorate is much less soluble in cold water than potassium chloride and is obtained in practice by this method, “fractional crystallisation”, as it is called, from the mixture formed by passing chlorine into a hot solution of caustic potash (see §§ 209, 576).

Where there is a very marked difference in solubility between two substances they are easy to separate in this way. Where the difference is slight the process is very tedious and must be repeated a large number of times before an approximately pure specimen of the less soluble ingredient is obtained.

95. The solubility of a salt is easily determined in practice by the method of Exp. 4. Or it may be done as follows. Weigh a clean evaporating dish. Place in it some pure saturated solution—i.e. solution which has remained in contact with undissolved salt for some time—free from any solid particles and weigh again. Evaporate to dryness. The loss in weight is the weight of water. The weight of salt dissolved in it is deduced by finding the

weight of the dish and its contents at the end of the experiment and subtracting from this the weight of the empty dish. The scheme sounds very simple. It is, however, easy to do it badly. The real difficulty lies in the later stages of the evaporation of the water, since the salt, as it gets dry, is apt to "spit"; small particles tend to break off and fly out of the dish. It is best to remove the last of the water by heating over a water bath. That is, the dish is placed over a vessel of boiling water. The finishing stages are thus slower, but accuracy is secured. The easiest case is that of a substance like common salt, which contains no water of crystallisation. By the time the water is all driven off, the dish has reached a constant weight; that is, further heating, cooling and weighing shows no further loss. Note here that in any chemical experiment nothing must be weighed while it is hot.

96. It is common to speak of substances as "soluble" and "insoluble". Many substances usually reckoned insoluble are, however, slightly soluble. Such things as chalk and sand dissolve to a small extent in water, and it is not improbable that even the most unlikely things do dissolve to a small extent.

97. Gases, like solids, dissolve in water, the degree of solubility varying very much. Under ordinary conditions 100 c.c. of water dissolve 1.5 c.c. of nitrogen, whereas water dissolves about 700 times its volume of ammonia. In the latter case, however, there is certainly some chemical action.

Unlike solids, gases are less soluble in hot water than in cold, and if a solution of a gas be boiled the gas is usually expelled. Gases are more soluble as the pressure increases. This is what one would expect. A familiar illustration of this is to be seen in the contents of any soda-water siphon. The gas in this case is carbon dioxide and it is forced into the water under pressure. The pressure in the siphon exerted on the surface of the liquid is several atmospheres. When the soda water is drawn off, the outside pressure being only one atmosphere, the gas is much less

soluble at the new pressure. The solution is reduced in strength to a saturated solution at the lower pressure. The liberation of the surplus causes the effervescence. The amount of a gas—that is the mass, and consequently also the weight—which can be dissolved under pressure is proportional to the pressure. If the pressure be doubled, for instance, the weight of gas which can be dissolved is doubled. If the reader lets his mind go back to Boyle's Law he will remember that at any temperature doubling the pressure of a quantity of gas involves halving the volume, so that at the doubled pressure the same *volume* of gas is dissolved as before. Thus a rule may be stated: *The volume of any gas which can be dissolved in a fixed quantity of a solvent is independent of the pressure.* This is known as **Henry's Law**.

98. It must be noted here that the pressure is the pressure of the gas itself. To see what this means, consider the cylinder in fig. 22. *A*, the lower part, contains a liquid, water for example. *B*, the space above the liquid, contains a gas, say chlorine. *P* is a piston head which can be moved up and down without any gas escaping from *B*. Now chlorine is soluble in water (see § 179) and so some of it will dissolve in *A*, and the pressure in *B* decreases. At last a stage will be reached at which the solution in *A* is saturated with chlorine at the pressure in *B* and at the temperature of the apparatus. If the pressure in *B* is increased by pushing *P* downward, more gas dissolves. There will then be a new strength of solution in *A* and a new pressure in *B*. These are proportional to one another. At twice the pressure, the solution is twice as strong; at three times the pressure, three times as strong, and so on. But if the pressure in *B* were raised by, say, pumping in air, no more chlorine would dissolve. True the pressure would be increased. But the total pressure in *B* would be partly due to chlorine and partly to air. We have seen (chap. III) that the resulting

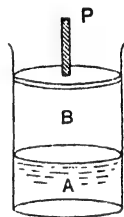


Fig. 22. Pressure and solubility.

pressures can be calculated by finding what would be the pressure if each gas filled the space alone and adding them up. Henry's Law applies to the partial pressure of the chlorine, not to the total pressure at the surface.

It will be seen that the law leads to the rather odd result that at no pressure every gas is insoluble in every liquid. This is true. So if there is no chlorine over the surface of a solution of chlorine to produce any pressure on the surface the gas starts to come off. In a closed bottle the pressure soon rises to a point such that the solution is saturated at that pressure. If the solution is left open to the air it will tend to get weaker and this will occur more rapidly if the gas which comes off is prevented from remaining over the surface by, say, a draught. This will not, however, continue indefinitely. The solvent itself evaporates, and in the case of a weak solution the dissolved gas may pass off and the solvent evaporate at such a rate that the solution remains at a steady strength, though, of course, diminishing in quantity. In fact, in the case of an *exceedingly* weak solution, the solution might conceivably get stronger. In any case the disadvantages of neglecting to replace the stopper in a bottle of such a solution are sufficiently obvious.

99. In the case of a very soluble gas there is a considerable contraction in volume when it dissolves. The act of solution has, however, in some way quite beyond our understanding, made the gas, to all intents and purposes, a liquid which can then be regarded as mixed with the solvent. We thus expect—and find—that when a liquid dissolves a gas there is an increase in volume of the solvent. For example, the density of the ordinary saturated solution of ammonia in the laboratory is 0.88. The density of liquid ammonia (that is, of the liquefied gas) is 0.62. The density of the solution is thus between this figure and the density of water, 1. If we mixed a liquid of density 0.62 and a liquid of density 1 we should expect the mixture to have a density intermediate between these two. A solution of ammonia

is in this respect not unlike the mixture we should expect to get if liquid ammonia and water could be mixed.

100. Two liquids may be able to be mixed together in any proportions, as, for example, alcohol and water, or they may not mix at all, as water and mercury. Sometimes, however, two liquids, when shaken together, do not form one homogeneous mixture, but each absorbs some of the other. Thus, if bromine and water be mixed they separate out into two layers, with the heavier bromine at the bottom. The water is then found to contain a little bromine and the bromine a little water. In such a case we speak of a solution of bromine in water and of water in bromine. The solubility of each liquid in the other, understood in this way, increases with rise of temperature, and a temperature may be eventually reached when the two solutions have the same composition. At this and higher temperatures the two liquids are miscible in all proportions.

101. When a gas dissolves in a liquid the molecules of gas are confined to the space occupied by the liquid, and if the gas is very soluble this means a considerable decrease in bulk. On the other hand, when a solid is dissolved in a liquid, the volume of solution is usually greater than that of the solid dissolved, as the latter occupies a larger space than before. Once the substance is in solution it does not matter whether it was originally a gas or a solid. Thus hydrochloric acid is a gas, oxalic acid is a solid. This difference in the original state ceases to matter so long as the acids are in solution.

Chapter XI

EQUIVALENT WEIGHTS. DULONG AND PETIT'S LAW. ATOMIC WEIGHTS

102. In § 70 it was stated that a chemical compound always contains the elements of which it is made up in the same proportions by weight. There is no evidence for any variation from this law, and it will be seen, on reflection, how well it is explained by the ideas of atoms and molecules, as stated in previous chapters. This agreement is so complete that a careless thinker sometimes slips into the habit of assuming that the "Law of Definite Proportions" in some way depends upon the atomic theory. This is putting the cart before the horse, for the law, being the result of observation, is true whatever theory may be held.

We shall now deal with some experimental facts about the law of definite proportions, and we can forget for the moment all about atoms and molecules while we notice the facts. We can then come back to our theory and see how the facts and the theory can be fitted in together, remembering always that if they cannot be so fitted in, then it is the theory which must be altered and not the facts.

103. In chap. v occurred an account of the action of sulphuric acid on zinc, hydrogen being given off. This is a *qualitative* result, i.e. it states what happens but does not consider the exact quantities of the substances involved. How much zinc must be dissolved in this way to give a gramme of hydrogen? To answer this a "quantitative" experiment must be performed.

The number of grammes of zinc required thus to give a gramme of hydrogen is called the **equivalent** of zinc. A more

precise explanation of the word "equivalent" will be given later in the chapter. The determination of an equivalent is a very important question, and the method by which the reader can find the equivalent of zinc is worth considering in some little detail.

The equivalent can be determined experimentally by dissolving a known weight of zinc in dilute sulphuric acid and measuring the volume of hydrogen evolved. The experimental details will be found in § 611. Since 22.4 litres of hydrogen weigh 2 gm., it requires no great mathematical gifts to find the weight of 1 litre of hydrogen, viz. 0.09 gm. Knowing, then, that the density of hydrogen is 0.09 gm. per litre at S.T.P., the weight of hydrogen displaced can be determined from the volume. From this we can calculate the weight of zinc which displaces 1 gm. of hydrogen.

Suppose 0.3 gm. of zinc gives 110 c.c. of hydrogen at 16° C. and 756 mm. pressure, collected in contact with water.

The pressure of aqueous vapour at 16° C. is 13 mm. of mercury, so the pressure of the hydrogen must be taken as 743 mm.

Let v c.c. be the volume of the hydrogen at 760 mm. and 0° C. Applying Boyle's Law and Charles' Law

$$\frac{v \times 760}{273} = \frac{110 \times 743}{289}. \quad \therefore v = \frac{110 \times 743 \times 273}{289 \times 760} = 101.6 \text{ c.c.}$$

If 1000 c.c. weigh 0.09 gm., this weighs

$$\frac{101.6 \times 0.09}{1000} = 0.00914 \text{ gm.,}$$

and is displaced by 0.3 gm. of zinc. Hence 1 gm. of hydrogen is displaced by

$$\frac{0.3}{0.00914} = 32.8 \text{ gm.}$$

This result is a little high. For our present purpose we shall take an approximate value, 32.5.

The experiment may be varied by altering the acid; the first important fact this brings to light is that the equivalent does

not depend upon the particular acid used. For example, hydrochloric acid can be used instead of sulphuric acid. Caustic soda will evolve hydrogen when it acts upon zinc, as was mentioned in chap. v, and this reaction also may be used to find the equivalent of zinc. The result is the same as before, viz. 32.5.

104. The experiment can be varied by using another metal, such as aluminium. The numerical result in this case is different. The equivalent of aluminium is found to be 9. But, just as for zinc, the same value of the equivalent is found, whatever the compound may be from which the aluminium displaces the hydrogen. It always requires 32.5 gm. of zinc to displace 1 gm. of hydrogen, 9 gm. of aluminium to displace 1 gm. of hydrogen.

Such experiments give the same result for the same metal, whatever acid—or alkali—is used. But before we take the number so obtained as a final determination of the equivalent of the metal let us consider a further point.

105. Many metals can readily be made to combine with oxygen, and we can usually find out by experiment how much of a metal, or other element, combines with 1 gm. of oxygen. For instance, we could weigh some zinc and oxidise it to zinc oxide by heating it in a current of air, special care being taken to collect all the zinc oxide produced. By weighing the zinc oxide obtained, we could find out how much zinc combined with 1 gm. of oxygen. Similar experiments could be performed with other metals and we could thus get a table showing how much of each of a variety of elements combines with 1 gm. of oxygen. We might call this a table of “oxygen-combination equivalents” (see Exps. 22, 23, 24).

For example, the hydrogen-replacement equivalent of zinc is 32.5. The oxygen-combination equivalent is slightly over 4, and in general it will be found that *the equivalents found by combination with oxygen are one-eighth of the equivalents found by replacement of hydrogen*. The reason for this is not difficult to see if we recall

the Law of Reciprocal Proportions (§ 72) and remember that in water 8 parts by weight of oxygen are combined with 1 part by weight of hydrogen. Many elements form compounds with oxygen but do not combine with hydrogen or displace it directly from an acid (e.g. copper). It is customary therefore to take 8 parts by weight of oxygen as the standard for combining or equivalent weights, instead of 1 part by weight of hydrogen.

106. Recalling again the Law of Reciprocal Proportions (§ 72) we see that we need not limit our definition of combining or equivalent weights to the quantities which combine with 8 parts by weight of oxygen or 1 part by weight of hydrogen. For example, it can be shown that 35.45 parts of chlorine combine with 1 part of hydrogen; if we determined the weight of a metal which combines with 35.45 parts of chlorine, that is its combining or equivalent weight. It is obvious that this principle can be applied with other elements.

We can then define combining or equivalent weights as follows:

The **combining weight or equivalent of our element** is the number of parts by weight of it which combine with or replace 1 part by weight of hydrogen, or 8 parts by weight of oxygen or the equivalent weight of any other element.

107. It will be noticed that the equivalent is a quantity obtained directly by experiment, and is thus independent of any theories we may form about the nature of chemical substances. The determination of the equivalent of zinc, for example, can be one of the very first chemical experiments a student performs. It thus differs from such quantities as atomic and molecular weights, which depend for their meaning on a particular chemical theory. It is barely conceivable—though unlikely in the extreme—that some future development of chemical theory might render the ideas of atom and molecule obsolete. But this could not alter the fact that the equivalent of zinc is 32.5, nor that this figure can be found both from the replacement of the

hydrogen of an acid and indirectly from the composition of zinc oxide.

108. Let us now return to the atomic theory and consider what connection there is between the equivalent weight and the atomic weight of an element. If the atomic theory is right, there should surely be some connection.

Let the reader make a first guess at the answer for himself. What is the most obvious suggestion? Take the case of zinc. The most obvious suggestion is surely that an atom of zinc replaces an atom of hydrogen, and since 32.5 gm. of zinc replace 1 gm. of hydrogen, the zinc atom weighs 32.5 times as much as the hydrogen atom. This suggestion is wrong, but there is no need for us with our accumulated knowledge to smile in a superior way at the error. We are convinced now that the atomic weight of zinc is not 32.5 but is 65, just twice as much. But why? If the reader happens to have gone over this ground before and is quite used to the statement that the atomic weight of zinc is 65, he may be surprised to find it no easy matter to explain exactly why, without any appeal to vapour densities.

If we go back a little in history we find the experimenters in, say, the year 1800, even more puzzled than we are. At that time, too, a knowledge of Avogadro's Law was not part of the mental equipment of every chemist. How did they tackle the problem? The equivalents presented no difficulty. How could they get from the equivalent to the atomic weight?

As a matter of fact, at that date there was great uncertainty about atomic weights. If zinc replaces hydrogen, atom for atom, then the atomic weight of zinc must surely be 32.5. But does it? Some metals, such as sodium or potassium, give two distinct sulphates, in one of which some of the hydrogen of the acid is replaced by the metal and in the other twice as much. This certainly suggests that there are at least two hydrogen atoms in a molecule of the acid which can be replaced by sodium one at a time. Zinc, however, only yields one sulphate. Shall we

say, then, that while one atom of sodium can replace one of hydrogen, an atom of zinc replaces two? If that be so, then the atomic weight of zinc would be not 32.5 but 65. The chemists at the dawn of last century had no fixed principle to guide them, no fixed method by which an atomic weight could be finally settled. There was much uncertainty and much argument about particular cases.

109. This state of affairs was cleared up by two French chemists, Dulong and Petit, who discovered a remarkable connection between the atomic weight of a solid element and its specific heat. We must leave the student to find out more about specific heat from his study of physics, merely stating here that the specific heat of a substance is the amount of heat necessary to raise the temperature of 1 gm. of it by 1° C. Dulong and Petit found by considering a large number of elements that as the atomic weight goes up the specific heat goes down and that the product, "*atomic weight multiplied by specific heat*", *remains about the same for different solid elements at approximately 6.4*. Thus the atomic weight of lead is 207 and its specific heat is 0.031. The product is 6.4. The law is only approximate, but this is not very important. Referring back to the case of zinc, for instance, we were not left in a position of total ignorance. Since the equivalent is 32.5 it is fair to expect, unless our ideas of atoms and molecules are all wrong, that the atomic weight is 32.5 or 65 or 97.5 or 130 or some higher multiple of 32.5, according to whether an atom of zinc replaces one, two, three, four or more atoms of hydrogen. Now the specific heat of zinc is 0.094. At a glance it is evident that 65 is the number which, chosen from the list above, fits in best with Dulong and Petit's rule.

But one point should be noted here and it cannot be noted too carefully. Dulong and Petit's Law was discovered by actually taking specific heats and atomic weights and multiplying them together. If there had not been a considerable number of atomic weights already known, Dulong and Petit could never have

noticed the law which bears their name. Before their time chemists had compiled a list of atomic weights, and there was much argument and much uncertainty as to its accuracy. The law of specific heats was only discovered because, for all its uncertainties, the list was in the main correct. The patient investigators before Dulong and Petit, who with so little to guide them got in so many cases so near to the truth, are really entitled to a very large share of the credit for this discovery. True the law did not fit every case. Yet it fitted so many that it seemed likely that, in cases where it did not fit, it was the atomic weight and not the law which was wrong. So a number of the atomic weights were corrected to fit the law. The result was a series of atomic weights mainly as we have them to-day. The results of the law have stood the test of experience, and, as always, that is the justification of it.

110. There are exceptions to Dulong and Petit's Law, notably carbon and silicon, for which the product "atomic weight \times specific heat" is a good deal too low. This may be because the exact conditions under which the specific heat should be measured are not known. If the specific heats of these two elements are measured at high temperatures the results are greater, and at very high temperatures the product is not far below Dulong and Petit's value of 6.4.

111. It is worth while trying to see exactly what Dulong and Petit's Law really means. To explain by an example, the atomic weight of iron is 56 and of gold 197. Their specific heats are 0.112 and 0.032 respectively. In each case the product is 6.3. That is to say that if we take 56 gm. of iron and 197 gm. of gold, each would require the same amount of heat, viz. 6.3 calories, to raise its temperature by 1° C. Now if the weights of an atom of iron and an atom of gold are in proportion of 56 to 197 we clearly must be dealing with the same number of atoms in each case. Hence the amount of heat necessary to raise the temperature of one atom of iron by 1° is the same as the amount necessary to raise

the temperature of one atom of gold by 1° . Thus Dulong and Petit's Law comes to this: that the amount of heat necessary to raise the temperature of one atom of an element by 1° is approximately the same for all solid elements. But the specific heat of a substance varies with the temperature, and one is inclined to suspect that if one knew the exact conditions under which this heat ought to be measured the amount would be not merely approximately but exactly the same.

112. To sum up, the atomic weight of a solid element can be found thus:

(a) Find the equivalent. Either this or a small whole number multiple of it is the atomic weight.

(b) Find the specific heat of the element and divide 6.4 by the result.

(c) Choose the multiple of the equivalent which is most nearly equal to the quotient in (b). This is the required atomic weight.

Notice how happily (a) and (b) work together. Both are necessary. (b) shows roughly the answer, as Dulong and Petit's Law is merely approximate. (a), on the other hand, gives us the choice of one of several quite distinct quantities which by taking care can be determined by experiment with great accuracy.

113. To take a simple example: A man is looking for a house in a long road of which all the houses are on one side. He has not been told the exact number, but knows that it is fifty something. He also knows that there is a lamp-post just outside the gate. With these two pieces of information, neither of which would identify the house alone, he can pick it out with confidence. Those numbered fifty something are, naturally, all in a block. Only one of them is opposite a lamp-post and this must be the house he wants. "Number fifty something" can be compared to the information supplied by Dulong and Petit's Law. The lamp-post marks the house definitely as one of several, well spaced apart at equal intervals, in the same way that the equivalent

settles that the atomic weight must be one of several numbers, namely the multiples of the equivalent.

114. The reader has now two entirely different avenues of approach to the practical problem of determining an atomic weight. The first is by the application of Avogadro's Law for determining *molecular* weights and then finding by analysis the least weight of an element that occurs in the gramme-molecule of a number—the larger the better—of compounds of the element. The second is by the application of Dulong and Petit's Law, depending on the determination of the equivalent and of the specific heat. The latter of these methods, be it noted again, is historically the older. For some elements, e.g. the so-called "permanent" gases, Avogadro's Law is the more helpful; for others, e.g. platinum, Dulong and Petit's Law is the more suitable. But there are several elements for which both methods are available. The close agreement of the values thus obtained, especially seeing that the two methods are so dissimilar, is a striking confirmation of the soundness of both.

Chapter XII

FORMULAE AND EQUATIONS

115. Now that the determination of atomic weights is better understood, we will keep our promise and return to the question of formulae, first introduced in our subject in § 77.

A chemical formula, such as " H_2O ", in the first place means a molecule of the substance it represents. **This is its primary and strictly correct meaning.** But it is also used sometimes as an abbreviation for the name of the substance. Some writers strongly object to this. We do not. It is a common habit of the laboratory and the lecture room, and he would be a bold chemist who denied that he had ever used such a phrase as "pass in H_2S " or "add dilute H_2SO_4 ". There is no use in being pedantically particular about it and we, at any rate, will not be shocked at any such expression.

Its formula is a summary of a great deal of information about a substance. The atomic weights of the elements have all been carefully found out by experiment, and a list of them with their symbols will be found on p. 473. By the aid of this list, and remembering that the molecular weight in grammes of any gas occupies 22.4 litres, we can deduce from its formula

- (1) The percentage composition of a substance (but see § 120);
- (2) The density of any gas (but see § 120).

116. Remembering also that chemical actions take place between the molecules, we can write down what happens in many chemical actions in the abbreviated form of an equation, on the left appearing the formulae of the molecules of the substances before the action and on the right the formulae of the molecules produced. If more than one molecule of a compound is necessary for the action, a number is placed before the formula to show this. Thus, $3\text{H}_2\text{O}$ means "three molecules of water". By the

principle of conservation of mass, the total number of atoms of an element must clearly be the same on both sides of the equation.

The formulae of the substances already mentioned in this book will be found on page 84. The list is arranged in the order in which the compounds occur in the text. They should all be noted and known. It is easy, now that chemistry is a well-established and well-investigated science, to write out such a list. But the establishment of even one of these formulae from first principles is no easy matter except in the very simplest cases.

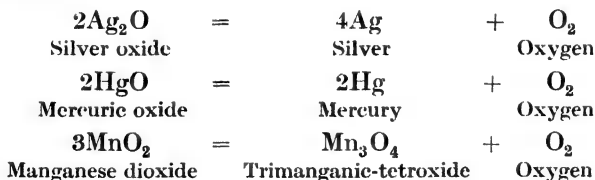
117. As examples of the uses of formulae and equations we shall now restate in the form of equations the reactions which were referred to under "Oxygen" and "Hydrogen".

Action of heat upon potassium chlorate, with or without manganese dioxide:



Notice that the oxygen is expressed as O_2 and not as O , since the oxygen is evolved in *molecules*.

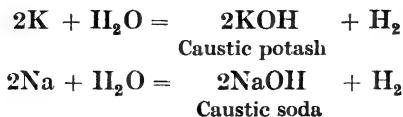
So also we have:



Combustion of phosphorus:



The equations for the action of metals upon water are:



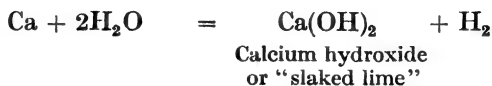
* Or P_4O_{10} (see § 388).

FORMULAE OF COMPOUNDS

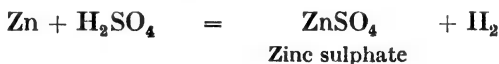
Iron rust—ferric hydroxide	FeO_2H_2 or $\text{Fe}(\text{OH})_2$	Zinc sulphate	ZnSO_4
Sulphuric acid	H_2SO_4	Nitric acid	HNO_3
Water	H_2O	Cupric oxide, or black copper oxide	CuO (the usual oxide of copper)
Salt—sodium chloride	NaCl	Carbon monoxide	CO
Silver nitrate	AgNO_3	Water gas	$\text{CO} + \text{H}_2$ (mixed)
Potassium chlorate	KClO_3	Sodium formate	NaHCO_2 or HCOONa (compare this with CH_3COOH , above)
Potassium perchlorate	KClO_4	Lead peroxide (brown)	PbO_2
Potassium chloride	KCl	Lead monoxide (yellow)	PbO
Manganese dioxide (or peroxide)	MnO_2	Copper oxide (red) or cuprous oxide	Cu_2O
Silver oxide	Ag_2O	Ferrous oxide	FeO
Mercuric oxide	HgO	Ferric oxide	Fe_2O_3
Lead peroxide	PbO_2	Sulphur trioxide	SO_3
Barium peroxide	BaO_2	Lead sulphide	PbS
Chromium peroxide	CrO_3	Ferrous sulphide	FeS
Nitrous oxide	N_2O	Copper sulphide	CuS
Magnetic oxide of iron	Fe_3O_4	Nitric oxide	NO
Sodium peroxide	Na_2O_2	Sulphur dioxide	SO_2
Potassium peroxide	K_2O_4	Alcohol	$\text{C}_2\text{H}_5\text{O}$ or $\text{C}_2\text{H}_5\text{OH}$
Calcium oxide (lime)	CaO	Marsh gas	CH_4
Copper sulphide	CuS	Benzene	C_6H_6
Calcium carbide	CaC_2	Carbon disulphide	CS_2
Barium oxide	BaO	Acetylene	C_2H_2
Acetylene	C_2H_2	Ethylene	C_2H_4
Carbon dioxide	CO_2	Propylene	C_3H_6
Hydrochloric acid (gas)	HCl	Caustic potash (potassium hydroxide)	KOH
Acetic acid	$\text{H}_3\text{C}_2\text{O}_2$, $\text{HC}_2\text{H}_3\text{O}_2$ or CH_3COOH^*	Calcium chloride	CaCl_2
Sodium hydroxide (sometimes called "caustic soda" or "sodium hydrate")	NaOH	Phosphorus pentoxide	P_2O_5
Zinc oxide	ZnO	Potassium permanganate	KMnO_4
Copper sulphate	CuSO_4	Silica or Silicon dioxide	SiO_2
		Calcium carbonate	CaCO_3
		Ammonia	NH_3

* The reason for these different ways of writing the formula will appear later (see § 397). CH_3COOH is the most usual and the best.

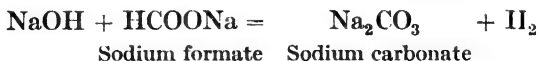
(Note. Sodium and potassium are much alike in their chemical properties (see § 506), so it usually happens that, when an equation can be written down for a reaction involving sodium, there is nearly always an exactly similar equation for a similar reaction involving potassium. The latter can be obtained from the former simply by putting K for Na. The two equations above illustrate this.)



Action of acids on metals:



Other reactions:



Combustion of sulphur and of carbon:

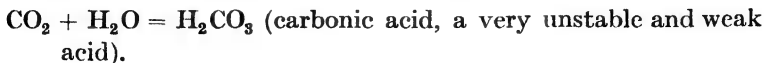


of zinc: $2\text{Zn} + \text{O}_2 = 2\text{ZnO},$

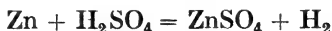
of aluminium: $4\text{Al} + 3\text{O}_2 = 2\text{Al}_2\text{O}_3,$

and so on.

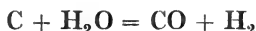
The oxides of sulphur, phosphorus and carbon act with water as follows :



118. In examining these equations, it should be remembered that they do not state the conditions under which the action takes place nor do they state whether the substances are solids, liquids or gases. The reader should refer back to chaps. iv and v and be quite sure he knows in which of these cases the action takes place at once, which require heating up to about boiling-point and which require considerable heat. For example:



represents an action which takes place easily with *dilute* acid and *impure* zinc and *without the application of heat*. The equation does not show this. Again, the action



requires the carbon to be *red hot* and consequently the H_2O to be in the form of *steam*. These facts do not appear in the equation. Further, the equations do not show whether the reactions produce or absorb heat.

119. In writing out such equations as these we usually know in the case of a gas how many atoms there are to a molecule but we have *no such knowledge in the case of a solid*. Hence, for example, silver is represented by Ag because we do not know whether the molecule of silver is Ag , Ag_2 , or whether the molecule contains any larger number of atoms. The formula of a solid or liquid is written in the simplest form unless we have real reason to believe it is more complicated.

120. It has already been stated that the percentage composition of a substance can be found from the formula. Notice that

here we are not deducing something we did not know before. In practice the percentage composition of a substance is known *before* the formula. The formula, however, enables us to recover it by a short calculation whenever required. So also in the case of the density of a gas. The density is known *before* the formula, but the latter is remembered and the density found from it when required.

Example: Calcium sulphate has the formula CaSO_4 . What is its percentage composition? (Atomic weights $\text{Ca} = 40$, $\text{S} = 32$, $\text{O} = 16$.) The molecular weight is clearly $40 + 32 + 4 \times 16 = 136$. That is, the "gramme-molecule" weighs 136 gm.

This contains 40 gm. of calcium.

Hence 100 gm. of calcium sulphate contain

$$\frac{100 \times 40}{136} = 29.4 \text{ gm. of calcium.}$$

So also we have

Sulphur 23.5 per cent.

Oxygen 47.1 per cent.

121. To illustrate the recovery of the density of a gas from the formula, suppose we wanted the density of the gas whose formula is N_2O^* ($\text{N} = 14$, $\text{O} = 16$). The molecular weight is $14 \times 2 + 16 = 44$, and the density, with hydrogen as the standard, is half the molecular weight, or 22. We also know that 44 gm., the gramme-molecular weight, occupies 22.4 litres at S.T.P., which enables us at once to calculate from weights to volumes and *vice versa*.

122. To find the simplest formula of a compound from the composition we proceed as follows:

Divide the weight of each element present by its atomic weight. The quotients are proportional to the numbers of atoms of each element present. Calcium chloride, for example, contains 36 per cent. of calcium and 64 per cent. of chlorine. What is its formula? ($\text{Ca} = 40$, $\text{Cl} = 35.5$.)

The relative weights of calcium and chlorine in the compound

* Nitrous oxide (see § 296).

are 36 of Ca and 64 of Cl. The relative numbers of atoms are obviously obtained by dividing these weights by the relative weights of the atoms (i.e. by the atomic weights).

Thus
$$\text{Ca} = \frac{36}{40} = 0.9$$

and
$$\text{Cl} = \frac{64}{35.5} = 1.8, \text{ nearly.}$$

The relative numbers of atoms are therefore one of calcium to two of chlorine.

The approximation is very close and small errors of this sort are to be expected in an experimental subject.

The formula is thus CaCl_2 , or some multiple of it, such as Ca_2Cl_4 , Ca_3Cl_6 , etc. We have seen that in the case of a solid there is often no way of settling which is correct and the simplest is chosen. If the density of the substance as a vapour can be found the point can be decided, but only for the vapour. We do not know that it is the same in the solid state, though we generally assume it is and no confusion results.

123. *When using equations for calculations, we always regard the formula of a substance as standing for a gramme-molecule of it. Consider for example the equation*



Referring to the list of atomic weights (p. 473), the equation conveys the information that "65 gm. of zinc dissolved in dilute sulphuric acid combine with 98 gm. of pure acid liberating 2 gm. (or 22.4 litres) of hydrogen and leaving 161 gm. of zinc sulphate in solution". With these numbers we can easily solve such problems as "How many grammes of zinc sulphate can be made from 12 gm. of zinc?" or "How much zinc is required to make 5 litres of hydrogen?" It is a matter of simple proportion. Note, too, how easily the transition from weights to volumes of gases is effected by the use of the fact *that the gramme-molecule of any gas occupies 22.4 litres at S.T.P.* (see § 65).

124. The history of the atomic hypothesis is not uninteresting. The idea is at least as old as the Greeks. Yet no definite progress was made in the establishment of the atomic theory until the time of Dalton, who seriously tackled the question of the evidence for it. He did not die until 1844, so it will be seen that the acceptance of the theory is not old.

The idea of the molecule does not go back anything like so far as that of the atom, although in our development of the subject the molecule is placed first. The molecule is a real and individual entity; the atom, as such, has no separate existence. To a speculator the atom comes more naturally, to an experimenter the molecule. This explains why the idea of the atom is older, and accounts for the precedence the molecule takes in modern chemical theory.

125. Dalton himself was wedded to the atom and did not accept Avogadro's explanations in terms of molecules. He was more interested in physics than in chemistry, and physics had not yet reached a stage which made the separate ideas of atom and molecule both necessary, whereas chemistry had already reached it. It was not until 1858 that Cannizzaro, of Rome, succeeded in securing the general recognition of Avogadro's work. Cannizzaro did not die until 1910. The fact that this date is comparatively recent emphasises the newness of the accepted chemical theory. A life which links Avogadro with the Curies* and radium has indeed seen chemical history.

* Pierre Curie (1859-1906) was professor of Physics at the Sorbonne. He was killed in a street accident in Paris—an accident which will cause no surprise to those familiar with the Jehus of that city. His wife, a Pole by birth, shared his scientific gifts and interests. Their discovery of radium ranks as a landmark in physics and chemistry, as they carried the subjects on a stage by showing that it is possible to break up the atom—at any rate in certain rare and peculiar cases—into something smaller. This completely revises our idea of the atom. Yet the reader need have no anxiety. For all practical purposes he may still treat the atom as permanent and indivisible. There are no reactions even remotely within reach of the ordinary worker which are exceptions to this.

Chapter XIII

VALENCY

126. To determine atomic weights it will be remembered that in the cases of many metals the equivalent is first found and that then by some further consideration—such as is provided by Dulong and Petit's Law—a small whole-number multiple of this equivalent is eventually picked out and adjudged to be the correct atomic weight. But it is not the same multiple for all metals. Had it been so, atomic weights would have been settled with less difficulty than they were. In the case of silver, the equivalent and the atomic weights are the *same*; in the case of zinc the atomic weight proves to be *twice* the equivalent weight; in the case of aluminium it is *three times*. These facts can be verified by experiment and by Dulong and Petit's Law. This small whole number by which the equivalent must be multiplied to get the atomic weight is called the "Valency" of the element. The idea of valency is of fundamental importance. We shall look at it a little more closely and then give a more complete definition of it.

127. The valency of a metal shows itself at once in the formulae of many of its simpler salts. For example, the formulae of a few salts already referred to are NaCl , AgCl , NaNO_3 , Na_2SO_4 , K_2SO_4 , ZnSO_4 , BaCl_2 , CaSO_4 . If these formulae are compared with those of the acids from which the salts are derived, it shows up clearly the fact that in the first five the metal has replaced the hydrogen atom for atom, whereas, in the others, *two* atoms of the hydrogen have been replaced by *one* of the metal. This marks a striking difference between the metals sodium, potassium and silver on the one hand and zinc, calcium and barium on the other. When aluminium is dissolved in hydrochloric acid, the chloride

formed proves on analysis to be represented by the formula AlCl_3 , *one* atom of aluminium displacing *three* atoms of hydrogen.

Now that we have met with the idea of valency this difference is only what we expect. These formulae should, however, be carefully noted at this stage, with the meaning of valency well in mind. A full and careful comparison of these salts with the metals and acids from which they are derived should prevent in many cases the writing down of unlikely or impossible formulae.

128. Of course these formulae were not originally derived from the valencies. The valencies had to be known before atomic weights could be determined and the atomic weights had to be determined before the formulae could be determined. So to get the valency of an element from a formula would only be justified in a case where we were quite sure the formula had been found without using any knowledge of the valency. A case where it is justified will be given later (see § 658).

129. Yet the valency of an element enables us to forecast with considerable success the formulae of many compounds before we ever meet them. Thus the usual valency of nickel is two, and the formula of oxalic acid is $\text{H}_2\text{C}_2\text{O}_4$. Hence it would be a great surprise to find that, if there is an oxalate of nickel, its formula were anything but NiC_2O_4 . But here, as always, the actual oxalate would have to be made and examined before it could be stated definitely that there is a substance of this formula. In most cases the formula is as expected. For example, taking the three common acids, HCl , H_2SO_4 and HNO_3 , the formulae of the potassium (valency 1), zinc (valency 2) and aluminium (valency 3) salts of these acids would be expected to be:



and



and so they are. Note, in particular, the formula of aluminium sulphate. Here two atoms of aluminium have replaced the six

atoms of hydrogen from the three molecules of sulphuric acid, i.e. each atom of aluminium has displaced three of hydrogen. Suppose, however, we tried to write down the formula of aluminium carbonate. Sodium carbonate is Na_2CO_3 and carbonic acid—a weak and unstable acid—thus appears to be H_2CO_3 . Aluminium carbonate would then be $\text{Al}_2(\text{CO}_3)_3$, but no such substance seems to exist.

130. It will be remembered that in § 106 the definition of equivalent was not confined to combination with or replacement of hydrogen but was extended to include combination with other elements. The definition of *valency* of an element may well be extended in a similar way:

(a) The number of atoms of hydrogen with which one atom of the element combines.

(b) The number of atoms of hydrogen which one atom of the element displaces from any compounds.

(c) The number of atoms of any element whose valency as defined by (a) or (b) is one, with which one atom of the element combines.

We have, then, three apparently different tests. The fact that any one of these three tests may be applied to decide a valency, and that the results so obtained are consistent, is a matter which depends upon experiment and experience. At the risk of being tedious this must as usual be insisted upon. The three tests are so consistent that by the time he gets used to them the reader will be almost tempted to forget that there *are* three.

The cases so far considered have come under test (b). The equivalent is determined directly; the valency is then settled either by Dulong and Petit's Law or by some other method, which comes to the same thing as settling how many atoms of hydrogen an atom of the metal has displaced.

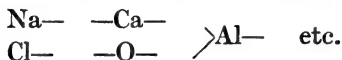
Test (a) is most useful in the cases of many non-metals. These often form compounds with hydrogen the formulae of which can be determined without difficulty. The reader should recollect

how this is done. If he has any doubt he should turn back to chaps. VI, VII and VIII and make himself quite clear on the point. In this way can be proved, for example, the formulae HCl (hydrochloric acid), H_2O (water), NH_3 (ammonia) and CH_4 (methane, the simplest of many compounds of carbon and hydrogen). So by test (a) the valency of chlorine is one, of oxygen two, of nitrogen three and of carbon four.

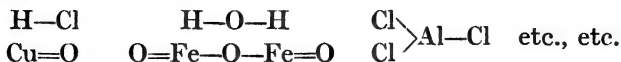
131. As an example of test (c), there is a compound of phosphorus and chlorine, phosphorus trichloride, with a formula which can be proved to be PCl_3 . This is *not* prepared by displacing the hydrogen of hydrochloric acid by phosphorus. Yet it can be used to justify saying that the valency of phosphorus in this compound is three, since one atom of phosphorus combines with three of the element chlorine, the valency of chlorine being one by test (a).

132. If the valency of an element is *one* the element is said to be "*univalent*",* if *two* "*bivalent*", if *three* "*trivalent*" or "*tervalent*", if *four* "*quadrivalent*", and so on. No element is known with a valency of more than eight.

133. Now suppose we represent an atom diagrammatically by writing down the symbol for it and drawing lines from it so that the number of such lines is the same as the valency, thus:



We can then represent a molecule by a "graphic formula" or "structural formula", with the atoms linked up by these lines, or bonds, thus:



* It used to be the custom to employ the Greek prefixes and to speak of elements being monovalent, divalent and so on. This has been abandoned, as it is considered preferable not to mix Greek and Latin roots in the same word. There are, however, quite a number of words which break this rule. For instance, to mention a word which is now becoming popular, "television".

It will be noticed that a bond always joins two atoms and never has one end free. Thus a compound of the formula HO (graphically —O—H) would be irregular, as it could only be represented with one of the two oxygen bonds unconnected to another atom, since hydrogen has only one bond. *Graphic* or *structural* formulae are of great utility and importance, and the student will be meeting with them constantly, especially in connection with compounds of carbon. It should be noted here that there are cases in which the same element has different valencies in different compounds. Thus the valency of iron may be two or three, that of mercury one or two, that of copper one or two. Of phosphorus and antimony the valency may be three or five, and of sulphur it may be two, four or six. Chlorine, bromine and iodine, already mentioned as univalent, are not always so. It will, however, be found as we proceed that these variations cause less confusion than might appear at first sight, and the reader will soon get used to the different valencies of the same element when he studies the elements to which these variations apply.

Chapter XIV

AIR AND NITROGEN

134. We have seen that *air is a mixture* of oxygen (21 per cent.) with an inert gas, **nitrogen**, and that the latter may be obtained by the simple process of removing the oxygen by the combustion of phosphorus or by passing the air over red-hot copper (see Exps. 28 and 29). Nitrogen is in striking contrast to the other gases we have studied. It does not support life or combustion. Nearly all the ordinary things which burn in air, when ignited and plunged into nitrogen, are immediately extinguished. Nor will it burn itself.

It is difficult to make nitrogen combine directly with anything, but nitrogen compounds are extremely important. *Proteins*, which always contain nitrogen, are amongst our indispensable foodstuffs, being most valuable ingredients in meat and also forming an important part of bread, beans and many other vegetable substances (see chap. XXIII). Nitrogen, in air, is very abundant, but its inertness makes it difficult for the chemist to make useful compounds of it. The utilisation of the nitrogen of the air is a very interesting and important modern chemical problem which we shall meet with again.

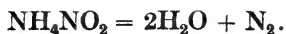
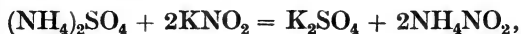
135. Nitrogen is a colourless, odourless, inert gas, nearly insoluble in water. It is fourteen times as heavy as hydrogen, so its molecular weight is 28. Its atomic weight is 14, and hence the formula is N_2 . It is thus a little lighter than oxygen. Air being a mixture of, roughly, four volumes of nitrogen and one of oxygen, its density ($H = 1$) is thus

$$\frac{4 \times 14 + 16}{5} = 14.4.$$

This calculation would not be valid if air were a compound.

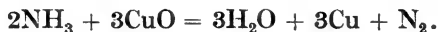
136. Nitrogen can be prepared by heating a mixture of ammonium sulphate and potassium nitrite (see Exp. 30).

This reaction produces ammonium nitrite, which immediately breaks up into nitrogen and water:

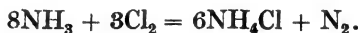


Nitrogen is **not** prepared by heating the salt ammonium nitrite by itself, as in this case the action is far too rapid to be under control and a **dangerous explosion would result**.

137. Nitrogen can also be obtained by oxidising ammonia, NH_3 . Thus if a stream of ammonia be passed over red-hot copper oxide, the reaction which takes place is expressed by the equation



138. Free nitrogen is also liberated on passing chlorine into a strong solution of ammonia. The ammonia *must* be in excess. The action proceeds thus:



The reader is emphatically cautioned not to try this method for himself, as it requires specially skilled handling. Excess of chlorine would result in the production of a dangerously explosive chloride of nitrogen, NCl_3 . Iodine, similarly, forms an explosive compound NI_3 , nitrogen iodide.

Methods for making nitrogen from its compounds are however of no practical interest. The air provides an ample supply of free nitrogen. It is the compounds of nitrogen which are of most importance, not the free gas. In studying an element, one of the first problems which presents itself is, "How can this element be prepared from its compounds?" And often the answer is so difficult that the element remains for centuries in its compounds unsuspected and unknown. But with nitrogen the emphasis is all the other way. The real question is not "How can I prepare

nitrogen from its compounds?" but "How can I prepare its compounds from nitrogen?" We have already promised that this important question will be faced later, when studying the compounds of nitrogen.

139. It was noticed by Lord Rayleigh (1893) that nitrogen made from air was appreciably denser than that evolved during a chemical action, as for example from ammonium sulphate and potassium nitrite. This suggested that the atmospheric nitrogen is not pure, but that it is mixed with another heavier gas, also chemically inactive. Now though nitrogen is very inert, metallic magnesium will burn in it, combining with it to yield a nitride (see § 618).

Using this fact, Sir William Ramsay succeeded in absorbing all the nitrogen by passing the gas over heated magnesium, and there still remained about 1 per cent. of the original bulk. This was a new gas, **argon**, far more inert even than nitrogen. No chemical compounds of it are known. Its molecule is monatomic. Its molecular and atomic weights are both 40 and its density is 20. Argon is now known to be one of a group of gases; the others are **Helium** (M.W. 4), **Neon** (20), **Krypton** (83) and **Xenon** (130). They are all as inert chemically as argon and all exist in small quantities in the atmosphere, though in the case of helium the amount in the atmosphere is only about five parts in a million. Helium, being light and non-inflammable, is very suitable for filling airships. It can be obtained with difficulty by heating certain minerals, e.g. uranium ores. In America it is obtained in larger quantities from certain natural gases. It is found also in the gas which escapes from radioactive waters, e.g. the mineral waters at Bath. Helium has been liquefied, its boiling-point being -268.7°C. , or $4.3^{\circ}\text{Absolute}$, and solidified at less than 1°Absolute (1926).

140. Two other ingredients of the air should be noted. One is **water vapour**. If some calcium chloride crystals be placed on a watch-glass and exposed to the air, they will absorb water and

become visibly moist. The other is **carbon dioxide** (see chap. XVIII). If air be bubbled through clear limewater it turns milky. This is a recognised test for carbon dioxide. The great importance of the carbon dioxide in the air will be seen in chap. XXIII. The quantity, however, is very small, 0·04 per cent.

Air being a mixture, the exact composition varies, but the following may be taken as a fair statement of the normal:

Oxygen	20·9
Nitrogen	78·1
Argon, etc.	1·0
Carbon dioxide about 0·04, or even less.	

Seeing that carbon dioxide is passed out in the breath of all animals, it is not surprising that the amount in the air varies considerably. For instance, in a badly ventilated room the proportion is much higher.

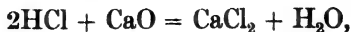
Chapter XV

ACIDS, BASES AND SALTS

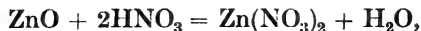
141. We have touched upon the subject of acids from time to time in the course of our study, and we shall now look at them a little more closely. The first fact the beginner learns about acids is that they turn blue litmus red (see § 35). Litmus thus provides a convenient method of *recognising* an acid, but the power of changing the colour of litmus is not the only distinctive feature of acids and is not by any means the most important. A man's finger-print can hardly be considered important in the ordinary way; yet it may be wonderfully helpful when it is necessary to recognise him. Notice, in passing, that an acid only affects litmus in the presence of water. This is true, not only of a gaseous acid like hydrochloric acid or a solid acid like oxalic, but also of a liquid acid like sulphuric. There is a real point to this fact, which will be revealed in chap. XXIX.

142. Acids, then, are an important class of compounds. Three of them, sulphuric acid, H_2SO_4 , hydrochloric acid, HCl , and nitric acid, HNO_3 , are among the most important substances in the laboratory. The essential thing about an acid is that it *contains hydrogen which can be replaced by a metal to form a salt*.

When discussing the preparation of hydrogen, it was seen how zinc sulphate and some other salts may be made directly from an acid and a metal. This is not, however, the commonest method of preparing salts. Another, and perhaps more usual way, is to dissolve an oxide in the acid. For example, calcium oxide (lime) can be dissolved in hydrochloric acid, when the action is



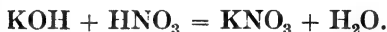
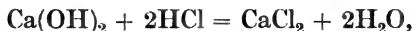
or zinc oxide in nitric acid:



with an exactly similar reaction for copper oxide.

It should be noticed therefore that the replacement of the hydrogen of an acid by a metal may be effected indirectly.

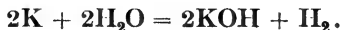
143. In these cases a salt is produced and also water. Oxides which dissolve in this way, giving a salt and water, are called **basic oxides** or **bases**. **Hydroxides**, another class of substances, are also regarded as bases. They yield a salt and water with an acid, but a *hydroxide* contains both *hydrogen* and *oxygen*. Compare the above reactions with



These equations show that in the case of a *basic oxide* the hydrogen in the water produced comes *entirely from the acid*; in the case of the *hydroxide half of it comes from the hydroxide*. If we compare these two classes of compounds with water we see that a basic oxide can be regarded as water in which *all* the hydrogen has been replaced by a metal, a hydroxide as water in which only *half* has been so replaced. Consider, for example, the two following simple reactions. When magnesium is heated in a current of steam the action which takes place is according to the equation



but when potassium is placed in cold water the action is



In these cases water acts to a certain extent like a weak acid, though it does not affect litmus. Such direct actions of water on a metal are not always practically possible (see chap. v).

144. The **alkalis** are an important class of hydroxides. These are hydroxides which are soluble in water and which turn

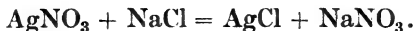
red litmus blue. They thus act in the opposite way to acids. This property, like the reverse property of an acid, is useful for purposes of recognising alkalis, but, as already explained, is not the most important thing about them. By far the commonest and most useful alkalis are potassium hydroxide, KOH, and sodium hydroxide, NaOH.

The reader should pause here, and before going on make sure he has a fairly clear idea of the differences between acids, basic oxides, hydroxides and alkalis. He will become more keenly aware of these differences as he reads on. In chap. XXIX he will find acids and alkalis discussed again from a new and very interesting view-point.

145. It was stated above that the replacement of the hydrogen of an acid by a metal results in the formation of a salt. A salt may be formed:

- (a) By direct action between an acid and a metal.
- (b) By action of an acid on a basic oxide or on a hydroxide.
- (c) By action of an acid on a carbonate. This is frequently a very good way to prepare the salt.

(d) By a double decomposition. This last method is very useful, more especially when the salt required is not soluble in water. If solutions of two salts of different bases and different acids are mixed, there is a tendency for the partners to be exchanged. If such an exchange results in the production of an insoluble salt it is deposited, and fine particles of a solid, called a *precipitate*, appear in the solution. It is an almost invariable rule to say that *if by such an exchange of partners a precipitate can be formed, it will be formed*. The reason for this is explained in § 423. One example of this—common salt and silver nitrate—was mentioned in chap. I. The action is

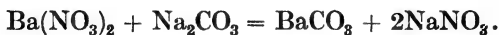


This “exchange of partners” is called **double decomposition**.

Thus if we want to make an insoluble salt, such as barium sulphate, BaSO_4 , we mix in solution a soluble salt of barium—e.g. BaCl_2 —and a soluble sulphate—e.g. Na_2SO_4 —and the BaSO_4 is precipitated and can be filtered off, washed and dried:



146. It is as well to notice here that practically all salts of sodium and potassium are soluble in water. Potassium tartrate, however, is only slightly soluble and potassium perchlorate not very soluble. Common chlorides are soluble except silver chloride, cuprous chloride and mercurous chloride. Lead chloride is soluble in hot water, but only slightly in cold. Common sulphates are soluble except those of barium, strontium and lead. Calcium sulphate is very slightly soluble. The common carbonates, except those of sodium and potassium, are insoluble. Being insoluble, carbonates are thus easily prepared, and when a salt cannot conveniently be made directly it is often easy to obtain it via the carbonate. Example: How could barium chloride be prepared from barium nitrate? If barium nitrate were mixed with hydrochloric acid or with the solution of a chloride, it would be difficult to obtain barium chloride from the solution, as everything present is soluble. So the solution of barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is mixed with sodium carbonate solution, when a white precipitate of barium carbonate is produced:



The BaCO_3 is filtered off, washed with water and dissolved in dilute hydrochloric acid:



If more BaCO_3 is used than the acid can dissolve, the excess filtered off and the filtrate boiled to expel the CO_2 , there remains a solution of BaCl_2 and nothing else. This preparation is typical of many and will repay careful consideration. It depends upon

Occasionally an acid occurs with a higher proportion of oxygen than that in the acid whose name ends in *-ic*; in such a case the prefix "per-" is used. For example HClO_4 is *perchloric acid*.

149. The names of salts of an acid ending in *-ic* end in *-ate*, and the names of the salts of an acid ending in *-ous* end in *-ite*. For example KClO_3 potassium *chlorate*, KClO_2 potassium *chlorite*, KClO potassium *hypochlorite*, KClO_4 potassium *perchlorate*. BaSO_4 is barium *sulphate*, BaSO_3 is barium *sulphite*, and so on. It will thus be seen that a compound whose name ends in *-ate* contains the elements named and oxygen. If the name ends in *-ite* again the compound contains the elements named and oxygen, but with less oxygen than the compound ending in *-ate*.

When the acids contain no oxygen the rules for naming them are simple. The acid carries the prefix "hydro-" but in the salt this prefix is dropped and the name ends in *-ide*. So we have HBr *hydrobromic acid*, AgBr *silver bromide*, and so on (compare this with § 33).

150. It frequently happens that a metal forms two series of salts with the same acid. In such cases the syllable *-ous* at the end of the name of the metal is used for the salt which contains the larger proportion of the metal in the molecule, the one with the smaller proportion of the metal being marked by the termination *-ic*.

Thus we have

FeCl_2 , *ferrous chloride* and FeCl_3 , *ferric chloride*,

SnS , *stannous sulphide* and SnS_2 , *stannic sulphide*,

and so on.

The student will, probably half-unconsciously, absorb in the course of his work many other points which crop up in connection with the naming of compounds.

Chapter XVI

TITRATION: ACID SALTS

151. If a quantity of acid, e.g. nitric acid, is placed in a beaker with a little litmus, and then a solution of an alkali, e.g. potassium hydroxide, is added drop by drop, the acid and alkali interact giving a salt and water, and there comes a stage as the alkali is added when there is just enough alkali to form a salt with *all* the acid present. If, for example, we refer back to the equation



we see (making use of the list of atomic weights on p. 473) that when 56 gm. of KOH have been added to 63 gm. of HNO_3 there is *no acid and no alkali left*. Up to this stage the litmus is red, but if any more alkali, even a single drop, be added, it turns blue. The litmus is thus used as an *indicator*.

It shows just when the right quantity of alkali has been added to neutralise *all* the acid. Other indicators, which may be used instead of litmus, are turmeric (yellow with acids, brown with alkalis), phenol-phthalein (colourless—intense red), methyl orange (red—yellow) and so forth. They are discussed more fully in § 636.

The above experiment is the basis of a very common and useful method of comparing the strengths of solutions of acids and alkalis.

A fixed amount—say 20 c.c.—of a solution of an alkali is placed in a beaker and a drop or two of litmus added. Then a quantity of acid is run in from a graduated tube called a “burette” (see fig. 23) and the number of c.c. necessary just to redden the litmus is noted. To

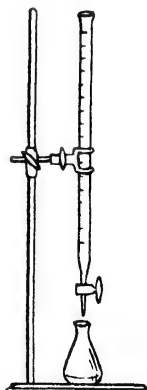
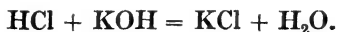


Fig. 23. Titration.

ensure accuracy about four trials are made and the average taken. From the equation, the strength of either solution can then easily be calculated if that of the other is known. The practical process is called a *titration*. An example will illustrate the method and its usefulness.

20 c.c. of hydrochloric acid is placed in a beaker with a few drops of litmus and solution of KOH is added drop by drop from a burette until the last drop turns the litmus blue. The experiment is repeated several times—say four—and the volumes of KOH required just to neutralise 20 c.c. of the acid are 4.7, 4.5, 4.6 and 4.6 c.c. respectively. If the KOH solution contained 2.9 gm. of KOH per 100 c.c., what was the strength of the HCl solution? The equation is



The average of the four quantities of KOH is 4.6 c.c.

100 c.c. of KOH solution contain 2.9 gm;

$$\therefore 4.6 \text{ c.c. of KOH solution contain } \frac{2.9 \times 4.6}{100} = 0.133 \text{ gm.}$$

56 gm. of KOH combine with 36.5 gm. of HCl;

$$\therefore 0.133 \text{ gm. of KOH combine with } \frac{0.133 \times 36.5}{56} = 0.087 \text{ gm.}$$

This is contained in 20 c.c. of the solution.

Hence 100 c.c. of the solution contain

$$\frac{0.087 \times 100}{20} \text{ gm. of HCl} = 0.43 \text{ gm.}$$

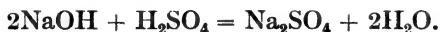
Ans.: There are 0.43 gm. of HCl per 100 c.c. of solution.

This is a simple and straightforward case. To work the calculation we require, in addition to the two volumes observed,

- (1) The equation;
- (2) The molecular weights involved;
- (3) The strength of *one* of the solutions (in grammes per c.c.).

152. This example is typical of many. It may be noticed as a practical detail that as the amount of KOH solution used is only measured to within 0.1 of a c.c. the possible error is about 2 per cent. If the solution were diluted with four times its volume of water, i.e. to one-fifth of its original strength, the error would still be in the neighbourhood of 0.1 c.c., but of the now weaker solution. The total error, considered as a weight, would thus be reduced to one-fifth of what it was in the question as put. On the other hand, with weaker solutions it is more difficult to detect the exact end-point of the reaction. Very strong and very weak solutions are thus both unsuitable for accurate titration, the former because a small error in volume means a fairly large error in weight and the latter because of this difficulty in seeing the end-point accurately.

153. Suppose two solutions be taken, one of sulphuric acid and one of caustic soda. Suppose, too, it has been determined by a careful titration how much of one solution will exactly neutralise a certain volume of the other. Once the proper quantities are known a neutral mixture can be made without the aid of any litmus, which would, of course, be an impurity in the final product. The equation for the reaction is



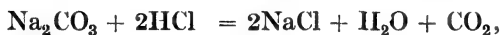
We are now in a position to effect this reaction without any excess of either ingredient.

154. Many other chemical actions, besides those between acids and alkalies, can be made the basis of a titration. The essential thing is to have some accurate way of determining the exact point at which the action is completed. This is usually done by some sort of colour change. In the cases of acids and alkalies considered the colour change takes place in the indicator. In some reactions, however, the colour change takes place in the substances themselves (see chaps. xxx, lv).

155. Titrating can be used in a very large number of cases for

investigating the quantities of substances present in a specimen. This branch of chemistry is termed **Volumetric Analysis**, and is distinguished from **Gravimetric Analysis** or the calculating of quantities by actual weighing in a chemical balance. These are apt to be regarded as quite separate and distinct branches of chemistry; but they are not really so. On a little reflection it will be clear that since the strength of at least one solution must be known (say, in grammes per litre) before any calculations can be worked out, there must be, at any rate, one solution of which the strength has been determined by actual weighing. The ordinary acids are difficult to procure pure. KOH and NaOH are both deliquescent, i.e. they readily absorb water from the air, and cannot easily be obtained dry. So such compounds are not very useful for making up a standard solution.

156. There are two particularly convenient substances available for this purpose. One is *sodium carbonate*, which can be fairly easily obtained pure and dry. It is readily soluble in water and dissolves in the commoner acids thus:



and so on. Sodium carbonate is alkaline to litmus and to methyl orange, although the formula suggests it ought to be neutral. This point is discussed more fully in § 458.

157. The other convenient substance is *oxalic acid*, a crystalline solid, which can be obtained cheaply in a very fairly pure state. It is specially useful as it can be titrated as an acid for ordinary acid and alkali titrations, or it can be used in a different class of reaction as a reducing agent (see § 491) and so will serve to standardise an oxidising agent such as potassium permanganate or hydrogen peroxide (see § 492). The way it is used in practice is described in chap. LV.

158. If a weighed quantity of sodium carbonate, say 5 gm., be

dissolved in distilled water and then more water added until the volume is, let us suppose, 1 litre, an alkaline solution of known strength is obtained. This can be used to find by titration the strength of a given solution of sulphuric acid, and this acid will then serve to determine the strength of an alkaline solution, say of KOH or NaOH.

On referring back to the equations, it will be noticed that on titrating sodium carbonate solution with an acid CO_2 is produced, some of which remains in the solution. This is feebly acid to litmus, and if litmus is used as the indicator the solution must be heated to expel it. It is better, however, to use as the indicator methyl orange, which is not affected by carbonic acid and so heating is unnecessary.

159. It will be convenient at this stage to extend somewhat the idea hitherto formed of an "equivalent". So far the term has been used only of elements and it should now be quite familiar to the reader that

$$\text{Equivalent} \times \text{Valency} = \text{Atomic weight.}$$

But the term "equivalent" is also used of a compound.

As is stated in §142, the distinguishing property of an acid is that it contains hydrogen which can be replaced by a metal. The equivalent weight of a metal is the weight which will (among other things) replace one unit weight of hydrogen. Similarly the equivalent of an acid is that weight of the acid which contains by weight one unit of replaceable hydrogen. But what kind of unit is this? A gramme? An ounce? A pound? It does not matter. No particular unit comes into the question. The equivalent of sulphuric acid is 49, because 49 gm. of the acid contain 1 gm. of hydrogen. But clearly, therefore, 49 tons of the acid contain 1 ton of hydrogen and so for any other unit. The equivalent is really the ratio of the weight of the acid to the weight of replaceable hydrogen it contains. The equivalent is thus a number, just as the molecular weight is. But just as we frequently

require the "gramme-molecular weight" of a compound, so, too, the "gramme-equivalent" is often useful.

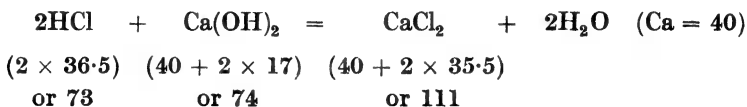
160. Coupled with the idea of the equivalent of an acid is the equivalent of a base. The equivalent of a base is the weight of the base which exactly neutralises the equivalent of an acid, the weight of the salt produced being the equivalent of the salt.

A little reflection here will show that:

(1) The "equivalent" of a base must be the molecular weight of the base divided by the valency of the metal it contains.

(2) The "equivalent" of a salt must also be the molecular weight divided by the basicity of the acid from which it is derived (see § 165).

To take an example, consider the equation for the action of hydrochloric acid on slaked lime:



The equivalent of HCl is clearly 36.5; it follows from the equation that the equivalent of Ca(OH)_2 is 37, and the equivalent of CaCl_2 is 55.5.

A dozen familiar examples should be written down at this stage and examined until the idea of an "equivalent" as applied to an acid, a base or a salt becomes as simple and familiar as the idea of the "equivalent" of an element.

161. A **normal solution** of a compound is a solution which contains the gramme-equivalent of the compound in 1 litre of the solution. (Note carefully that this is not the same thing as saying "the gramme-equivalent . . . in 1 litre of water". This would ignore the important fact that the substance dissolved occupies some space.)

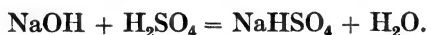
A normal solution (often written "*N*") is a strong one. Many salts generally considered as soluble in water are not soluble

enough to give a normal solution. It is more usual to work with a solution one-tenth as strong as a normal solution; this is called a **deci-normal** solution and is written $N/10$. Thus " $N/10 \text{ H}_2\text{SO}_4$ " on a bottle means that the liquid in the bottle is dilute sulphuric acid containing 4.9 (i.e. one-tenth of one-half of 98) gm. of pure H_2SO_4 per litre. Similarly $N/2$ would mean a semi-normal solution, $N/100$ a centi-normal solution (i.e. one-hundredth of the strength of a normal solution).

162. If a quantity of an acid is exactly neutralised by a quantity of a base and the two substances are both in normal solutions (or both in $N/10$ solutions) the volumes required will be equal, as the reader should easily be able to see for himself. It is this simplification which makes normal or deci-normal solutions useful.

163. Let us now return to the simple case of an acid and alkali titration, using a solution of caustic soda, NaOH , and dilute sulphuric acid. For our immediate purpose the strength of neither solution need be known.

Suppose it is found that 20 c.c. of the alkali exactly neutralises 50 c.c. of the acid. Let the 20 c.c. be mixed with *twice* the quantity of acid necessary to neutralise it, i.e. with 100 c.c., as is done in Exp. 47. That experiment yields, on evaporating off the water, **sodium hydrogen sulphate** or **acid sodium sulphate**. The action is:



This salt is acid to litmus. Such salts can be produced from any acid which has more than one replaceable hydrogen atom in the molecule, though they are not always acid to litmus. Sodium hydrogen sulphate is also called **sodium bisulphate**. Similarly there are bicarbonates (e.g. NaHCO_3), binoxalates (e.g. KHC_2O_4), etc. Note, however, an important exception. Chromic acid is H_2CrO_4 and potassium chromate is K_2CrO_4 . The salt usually called potassium bichromate is $\text{K}_2\text{Cr}_2\text{O}_7$. The nomenclature is

not consistent. To regularise this we shall call $K_2Cr_2O_7$, "potassium *dichromate*". The reader will find it helpful to compare *basic oxides* with *normal salts* and *hydroxides* with *acid salts*, considering them as derived from water and acids respectively.

164. The point here may be summed up as follows. When an acid contains two atoms of replaceable hydrogen, a univalent metal can form two salts, one (the normal salt) by replacing *both* hydrogen atoms by *two* atoms of the metal and the other (the acid salt) by replacing only *one* by *one* atom of the metal. An atom of a bivalent metal replaces both atoms of hydrogen and can form only one salt, the normal salt. So there are, for example, two potassium sulphates— K_2SO_4 and $KHSO_4$ —and only one zinc sulphate, $ZnSO_4$. It will be recollected that the fact that zinc and some other metals form only one sulphate, whereas sodium, for example, forms two, was one of the facts to which the reader's attention was drawn when considering the differences between the chemical behaviour of these metals and which led on to the idea of differences in valency (see § 108).

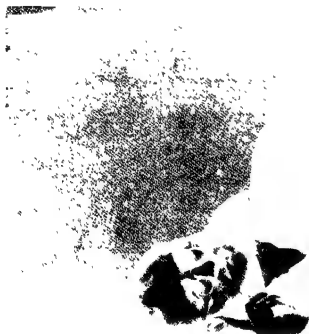
165. The number of replaceable hydrogen atoms in a molecule of an acid is called its **basicity**. Thus the basicity of hydrochloric acid and nitric acid is one (the acids are described as **monobasic**), that of sulphuric acid is two (and the acid is **dibasic**). The basicity may be more. Phosphoric acid, for example, is **tribasic**. The formula is H_3PO_4 and three different sodium phosphates are known, Na_3PO_4 , Na_2HPO_4 and NaH_2PO_4 (see § 390).

166. It should be noted that an acid may contain other hydrogen atoms in the molecule which cannot be replaced by a metal and which are in no way connected with its acid properties. For example, acetic acid is $HC_2H_3O_2$, more usually written CH_3COOH , only one hydrogen, the last, being replaceable by a metal. There is only one sodium acetate, and it is written CH_3COONa ; the non-replaceable hydrogen is for convenience written separately. It may be remarked in passing that there are

JOSEPH PRIESTLEY
Discoverer of Oxygen and of Nitrous Oxide.



JOHN DALTON
Who stated the Atomic Theory.





JACOB BERZELIUS

Who stated the Law of Multiple Proportions.



LOUIS JOSEPH GAY-LUSSAC

Who stated the Law of Gaseous Volumes.



SIR HUMPHRY DAVY

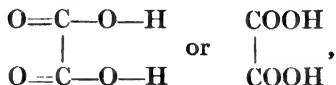
Discoverer of Sodium and Platinum.



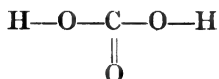
MICHAEL FARADAY

Who stated the Laws of Electrolysis.

a very large number of organic acids—i.e. acid compounds of carbon—which contain a group which may be written (using the method described in § 133) thus: $\begin{array}{c} \text{O} \\ \diagup \\ -\text{C} \\ \diagdown \\ \text{O}-\text{H} \end{array}$, or more briefly —COOH. Two of these have already been mentioned, viz. oxalic acid, which may be written



and carbonic acid, the acid present in a solution of carbon dioxide, which can be written



It is important to notice that there are four chief types of salts.

Normal salts, which are salts obtained by the replacement of all the *replaceable* hydrogen of an acid by a metal (or radical, such as ammonium NH_4). They contain no replaceable hydrogen, and no replaceable oxygen or hydroxyl, e.g. Na_2SO_4 , ZnSO_4 .

Acid salts, which are salts obtained by the replacement of only part of the replaceable hydrogen of an acid, e.g. NaHSO_4 , NaHCO_3 .

Basic salts, which contain oxygen or hydroxyl which can be replaced by an acid radical with the formation of a normal salt, e.g. BiOCl , which reacts with hydrochloric acid to form the normal salt BiCl_3 .

Many basic salts are compounds of one or more molecules of a normal salt with one or more molecules of the base, e.g. $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$.

Double salts, which are compounds of two or more salts, often combined with water of crystallisation, e.g. alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, and ferrous ammonium sulphate,

$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. These are definite compounds of invariable composition (see § 9) but they behave chemically like a mixture of the constituent salts.

It should be noticed that potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, is not a double salt; it does not possess the properties of an iron salt or of a cyanide; it is the potassium salt of hydro-ferrocyanic acid, $\text{H}_4\text{Fe}(\text{CN})_6$ (see § 460).

Chapter XVII

THE HALOGENS:

CHLORINE, BROMINE, IODINE, FLUORINE

167. With the elementary gases studied so far—oxygen, hydrogen and nitrogen—the non-scientific public usually has a nodding acquaintance. Chlorine, another elementary gas, is a little less generally known. It was discovered by Scheele, a Swede, as far back as 1774, and was for some time thought to contain oxygen. It was not till 1810 that Davy concluded that it was an element.

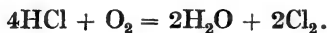
Chlorine forms a natural group with three other elements—fluorine, bromine and iodine. These four elements are called “halogens”. They were originally grouped together because their properties are somewhat similar, especially those of chlorine, bromine and iodine. At first this similarity was regarded as just a coincidence; but the reader will discover by slow degrees as he proceeds that there is a scientific reason for this grouping. For the moment, however, we shall take it as simply an interesting fact discovered by observation.

168. Chlorine is exceedingly plentiful in nature. It is not found in a free state, but in combination with metals, particularly as common salt, sodium chloride. Other common compounds of chlorine are potassium chloride—in sea water and as mineral crystals of *sylvine*—and *carnallite*, a double chloride of magnesium and potassium, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Most chlorides being soluble in water they are only found as solid minerals under special circumstances, such as the drying up of a saline lake. Silver chloride is insoluble and is one of the ores of silver, and is known as “horn silver”.

169. There are several ways of preparing chlorine, but they

resolve for the most part into two—oxidation of hydrochloric acid and electrolysis.

Hydrochloric acid, HCl , when oxidised yields chlorine. The oxidation may be direct. A mixture of oxygen (or air) and hydrochloric acid gas is passed over hot bricks, soaked in a solution of cupric chloride. It is found that the copper chloride acts as a catalytic agent and about four-fifths of the hydrochloric acid is decomposed:



This method was used industrially and is known as the "Deacon Process".

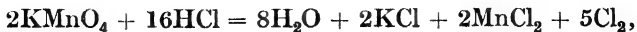
170. The more common laboratory methods are less direct (see § 650). If almost any oxidising agent is heated with strong hydrochloric acid, chlorine is evolved. It is customary to use manganese dioxide for the purpose, when the action is



171. The gas is heavier than air and is soluble in water. It is thus best collected by passing it down into a gas jar, the air being displaced upwards. The apparatus is as in fig. 24.

Chlorine cannot be collected over mercury, as it attacks it chemically. It can, however, conveniently be collected over *hot* water.

172. Other convenient oxidising agents for use in preparing chlorine are potassium permanganate and lead peroxide. The equations are



In the case of potassium permanganate the action takes place

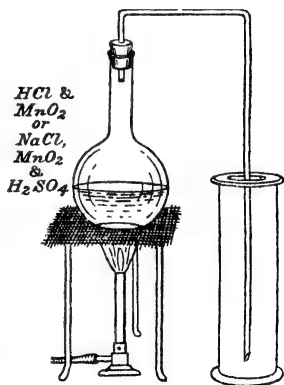
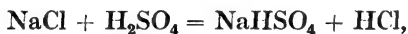


Fig. 24. Preparation of Chlorine.

without any heating. Chromium trioxide, hydrogen peroxide, sodium peroxide and other oxidising agents can also be used. In fact the emission of chlorine on treating with hydrochloric acid (heating if necessary, as it usually is) is a good test for an oxidising agent (see § 463), the chlorine evolved being recognised by its smell and its bleaching properties (see § 180).

173. Manganese dioxide and hydrochloric acid were formerly used on a large scale to produce chlorine in the Weldon process. The actual method of making the chlorine is as already described, the distinctive point of the Weldon process being the recovery of the manganese dioxide. This was done by mixing slaked lime, Ca(OH)_2 , with the manganese chloride produced, and blowing air through the mixture. A deposit having the composition CaOMnO_2 is formed, and this can be used instead of fresh manganese dioxide. Thus the manganese, the most expensive ingredient, is not wasted but is used again and again.

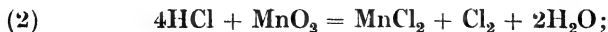
174. It is sometimes convenient to produce the hydrochloric acid and then oxidise it in one process. The ordinary action of sulphuric acid on common salt is expressed by the equation



or, if more salt be used and the mixture heated to about 500°C. ,



If then manganese dioxide, or other suitable oxidising agent, be mixed with common salt and strong sulphuric acid added and the whole heated, the hydrochloric acid is at once oxidised and chlorine is evolved. No manganese chloride remains, as it is acted upon by sulphuric acid. The action may be expressed in stages thus:



And the hydrochloric acid produced in (3) is decomposed by more manganese dioxide. The whole is effectively expressed by the equation



or



In actual practice both the sulphate and the acid sulphate are usually produced (i.e. the reactions represented by both equations occur), the quantities used and the temperature deciding how much of each, a high temperature and excess of salt being favourable to the production of the sulphate Na_2SO_4 .

175. Most of the chlorine of commerce is produced by electrolysis. The simplest method is the electrolysis of fused common salt (see § 509). This is a method of making metallic sodium, the chlorine being then of secondary importance:



The heat produced by the current keeps the salt melted. No water is present.

176. If a *solution* of common salt is electrolysed, chlorine is evolved at the anode and the sodium liberated at the kathode at once forms caustic soda and hydrogen (see § 513). By a modification of this process caustic soda is produced on a large scale, the chlorine again being a by-product. Chlorine is soluble in water, but the solution soon becomes saturated, after which the chlorine is evolved freely.

177. Of the three technical processes mentioned—the Deacon process, the Weldon process and the electrolytic method—the third is now by far the most usual. The reason will be clear. Many thousands of tons of electrolytic caustic soda are made annually and the chlorine evolved supplies more than half the world's needs. The chlorine must inevitably be cheap, as the makers of the caustic soda by electrolysis must of necessity

produce it in huge quantities and it must be disposed of somehow. They cannot throw it away; this would contaminate the air for miles around. To absorb it would be expensive. The simplest course is to sell it for bleaching purposes. It is usually liquefied by cold and pressure and stored in steel vessels and marketed in this form. The two older processes are naturally becoming continually of less importance as the electrolytic method of making caustic soda becomes more and more general.

178. Chlorine is a greenish yellow gas; it derives its name from the Greek word for its colour. The student may recognise the same root in the name of the green colouring matter of plants, chlorophyll. Chlorine has a most characteristic choking and irritating smell. The first poison gas used in the Great War was chlorine.

179. The atomic weight of chlorine is 35.5 and its molecular weight 71. Hence the molecule is written Cl_2 . A volume of water at ordinary temperatures dissolves about twice its volume of chlorine. The solution is known as chlorine water. On cooling to freezing-point a solid compound of chlorine and water, chlorine hydrate, separates out.

180. A good many of the chemical properties of chlorine are easily understood by remembering that chlorine has a considerable affinity for hydrogen, which is the scientific way of saying that chlorine and hydrogen readily combine. Thus a dilute solution of chlorine water, when exposed to the light, slowly evolves oxygen:

$$2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2.$$

Hypochlorous acid, HClO , is also formed during the action, but this decomposes in sunlight: $2\text{HClO} = 2\text{HCl} + \text{O}_2$.

Chlorine readily bleaches many organic colouring matters. This, again, is due to its affinity for hydrogen. The bleaching only takes place when moisture is present, the chlorine as before combining with the hydrogen in the water and the liberated oxygen attacking and destroying the colouring matter. Thus an

ordinary coloured flower placed in chlorine is bleached white. This fact is of practical importance as will be explained later.

181. Many substances burn in chlorine, the combustion being of two distinct types. If a piece of blotting paper dipped in warm turpentine be put into a jar of chlorine, it catches fire and burns with a dull smoky flame. Turpentine is a compound of hydrogen and carbon. The chemical action consists in the combination of the chlorine with the hydrogen. Heavy fumes of hydrochloric acid are produced, and the carbon liberated is deposited as soot. The action is in sharp contrast with the burning of turpentine in oxygen, when the flame is very bright and white. A candle burns in chlorine much as turpentine does.

182. Chlorine does not combine directly with hydrogen in the dark. In sunlight or any very strongly actinic light, however, a mixture of chlorine and hydrogen explodes violently and hydrochloric acid is formed. Hydrogen will burn quite easily in an atmosphere of chlorine. In these cases the chlorine combines with hydrogen. Combustion of a rather different type occurs when many metals are burned in chlorine; direct combination of the metal and chlorine takes place and a chloride is formed. Copper, lead, tin, iron, to mention a few, are metals which when finely divided catch fire in chlorine and form chlorides in this way. Phosphorus also catches fire in chlorine and forms the chloride PCl_3 , or, in excess of chlorine, PCl_5 .

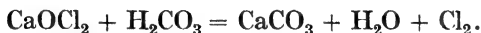
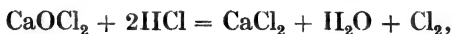
183. Chlorine was the first gas to be liquefied (by Northmore in 1806 and independently by Faraday in 1823). It can be liquefied at ordinary temperatures by the application of pressure. Northmore's method consisted in heating chlorine water in a sealed tube. When this is done chlorine is evolved, and as the pressure increases the gas liquefies. Liquid chlorine does not mix with water, and being heavier forms a separate layer in the tube. The liquid can be stored in an ordinary soda-water syphon. Much of the chlorine used for practical purposes is, however, not stored as free chlorine but combined as bleaching powder.

This is a compound formed by passing chlorine over dry slaked lime, Ca(OH)_2 (calcium hydroxide). The essential part of the action is represented thus:



Bleaching powder is, however, not pure CaOCl_2 . It contains some unchanged calcium hydroxide. It is sometimes referred to as "chloride of lime".

Almost any acid—even such a weak acid as carbonic acid—acts upon bleaching powder, liberating chlorine, thus:



184. Chlorine is often used either free or as bleaching powder to bleach vegetable fabrics, such as cotton or flax (linen), the natural product not being a pure white. When bleaching powder is used the fabric is first cleaned by boiling in dilute alkali (NaOH) and then treated with bleaching powder in the cold. It is next immersed in very weak hydrochloric acid when chlorine is liberated which bleaches the material as already explained. All traces of chlorine are afterwards removed by very thorough washing. The addition of a little sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), which combines with chlorine, ensures this. Note that chlorine is not used for bleaching animal fabrics, such as wool or silk. Nor is it used for straw. It is a matter of experience that it is unsuitable in these cases, the chlorine being found to act destructively on the fabric.

185. Chlorine is used as a disinfectant. It is very effective in killing germs, and its power of oxidising, which is so readily seen in its bleaching properties, also destroys many kinds of offensive organic matter.

186. Bromine is a heavy red liquid, found in nature in combination with sodium or potassium in sea water and certain salt deposits. There was, until recently, a large store of untouched

bromides in the Dead Sea, and schemes have in the last year or two been set on foot to work it (see § 508). The atomic weight of bromine is 80. It has an unpleasant odour, not unlike that of chlorine, and it also acts as a feeble bleaching agent. The vapour density corresponds to the formula Br_2 , though, of course, this gives no clue to its molecular state when liquid. It causes great irritation if it touches the skin and so must be handled with care.

187. Iodine is a grey-black solid, resembling black lead in appearance, which on warming turns to a beautiful violet vapour. The name iodine is derived from the Greek word for the colour violet. Iodine melts at 114°C . and boils at 184°C . It vaporises rapidly even below its melting point (see § 188). The atomic weight is 127. The formula for the vapour is I_2 when it is first vaporised, but if the vapour be considerably heated it dissociates until at very high temperatures all of the diatomic molecules (I_2) have been split up into monatomic molecules (I) (see § 441). Iodine is only slightly soluble in water, but it readily dissolves in a number of other liquids, some of the solutions being brown, as, for example, the familiar "tincture of iodine", and others violet. The tincture is a solution in alcohol and is used as an antiseptic for cuts, etc. Iodine is very soluble in a water solution of potassium iodide, again yielding a brown solution. The most familiar purple solution is the solution in carbon disulphide, CS_2 (see § 373). Iodine yields an intense blue colour with moistened starch; this is a very sensitive test and is much used.

188. Iodine in combination occurs in sea water and in certain salt deposits. It is much rarer—and so more expensive—than bromine. It can be made from "kelp", a sea weed which is collected for the purpose. Kelp contains potassium iodide, which remains in the ash after the weed is burnt. Most of the iodine produced nowadays has a mineral origin and is made from sodium iodate which occurs as an admixture in the nitrate beds in South America to the extent of about one part in 500. The

mineral is dissolved in water and then crystallised by evaporation. In this way purer NaNO_3 is obtained, the NaIO_3 remaining in the "mother liquor". Iodine is precipitated from this by treating it with a solution of sodium bisulphite, NaHSO_3 . The principal reaction is:



The iodine is filtered off, partially dried by pressing it and then purified by sublimation. "Sublimation" is a process just like distillation, except that the term is applied to the case of a solid which turns to a vapour and back to a solid without there being any liquid phase in between. In other words the solid "boils before it melts".

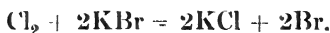
189. Iodine in small quantities is essential to good health in man and the higher animals. The secretion of the thyroid gland in the neck contains a complicated compound of iodine, and iodine is used in medicines in the treatment of thyroid diseases. Household salt is frequently "iodised", i.e. a small quantity of an iodide is mixed with it. This helps to supply the body with the iodine it requires and iodised salt is becoming very popular as an aid to good health. The taste of the salt is not affected.

190. Both bromine and iodine can be prepared in a similar way to chlorine (see §§ 170, 171). A bromide or iodide is mixed with manganese dioxide and sulphuric acid and then heated. Bromine is distilled off. Iodine, on heating, sublimes. It is easily condensed on a cold surface to black shining crystals:



The equation for iodine is similar. The equation can be modified, as for chlorine, for the case where the salt K_2SO_4 is formed. In practice there is usually an excess of acid, and the above equation represents what actually takes place.

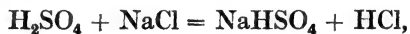
191. Chlorine will at once replace bromine or iodine from a solution of a bromide or iodide:



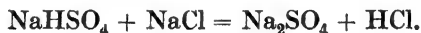
So also bromine will replace iodine. This can be used as a test for a bromide or iodide in solution. If a little carbon disulphide be placed in a solution of an iodide, it forms an oily drop at the bottom. On passing in a stream of chlorine or adding chlorine water the iodine is liberated, which dissolves in the disulphide and colours it violet. If a bromide be used instead of an iodide, the drop is stained red. Bromine is quite commonly manufactured from a bromide by treatment with chlorine.

192. Chlorine, bromine and iodine all form acids with hydrogen only, HCl , HBr , and HI . All three are gases, very soluble in water.

We have seen that sulphuric acid acting upon common salt liberates gaseous hydrochloric acid (see § 174):



and with more salt and upon heating:



In the laboratory the first stage is all that is necessary, but on a large scale the reaction is made to go to the second stage to avoid waste of acid. The gas evolved is colourless, but on meeting with the moisture in the air it becomes visible, like steam. It is a little heavier than air and can be collected by passing it downwards into a jar to replace the air. This must be done, however, in a draught cupboard as the gas is a corrosive poison. This method is the common commercial method of obtaining HCl , and is now a commercial process. (See Plate III, where the hydrogen is burning in silica burners.) The production of hydrochloric acid directly from hydrogen and chlorine has already been referred to (see § 182).

193. Hydrochloric acid as sold commercially contains 32 per cent. of hydrogen chloride (about 237 volumes of gas to 1 of water). If this solution is heated, the vapour contains a higher proportion of hydrogen chloride and a less proportion of water than the solution, which thus becomes weaker, until a solution containing 20·2 per cent. of hydrogen chloride is

obtained, which then distils unchanged at 110°C . If a solution which is weaker than 20.2 per cent. is heated, the vapour contains a higher proportion of water and a less proportion of hydrogen chloride than the solution, which thus becomes stronger until the constant boiling mixture is obtained, containing 20.2 per cent. and boiling at 110°C .

194. The composition of hydrochloric acid gas by volume can be established as was that of water (see chap. ix). If equal volumes of chlorine and hydrogen are exploded together, the resultant gas occupies the same volume at N.T.P. as the mixture did before the explosion. Hence the equation for the action is $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$, the formula being HCl . If we look at the equation we shall notice that there are the same number of molecules on the left as on the right, i.e. it expresses the fact that the volumes of the gases before and after the experiment are the same. If a molecule of hydrochloric acid were more complicated than the formula HCl indicates, there would be a contraction in volume when the hydrogen and chlorine combined. The absence of any such contraction justifies the formula HCl .

195. A solution of the acid can also be split up by electrolysis into chlorine and hydrogen. The anode, where the chlorine is liberated, must be of carbon, as the chlorine would attack a metal, even platinum. The action is started and allowed to continue until the solution is saturated with chlorine. After this the gases can be collected and measured and the volumes are found to be equal.

196. The hydrochloric acid used in the laboratory is a water solution, and this water solution is commonly referred to as hydrochloric acid. It is a very useful reagent and one of the most powerful of acids. Many metals dissolve in hydrochloric acid. Zinc, iron, magnesium and aluminium dissolve easily. Tin dissolves in hot and concentrated acid. Lead and copper are only slightly acted upon when the acid is dilute. Copper is only attacked in the presence of air. Boiling hydrochloric acid acts

upon lead, giving the chloride, PbCl_2 . In each case the chloride is formed and hydrogen liberated, in the case of iron the chloride formed being ferrous chloride, FeCl_2 . Chlorides can also be produced by direct union of chlorine with the metal, but in the case of iron this method gives ferric chloride, FeCl_3 . A chloride can, however, be more conveniently made by dissolving the carbonate or hydroxide or oxide of the metal in hydrochloric acid. In this way a solution is obtained, from which the salt may be obtained as crystals by heating until most of the water evaporates and then allowing the salt to crystallise out.

197. The anhydrous salt cannot always be prepared in this way, as heating to dryness may decompose the chloride. For example, magnesium chloride is easily obtained as crystals with a composition expressed by $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. On heating to dryness some of the chloride acts upon some of the water, thus:



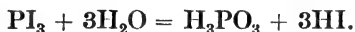
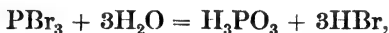
and the gaseous hydrochloric acid is driven off. The result is a mixture of MgO and MgCl_2 . The anhydrous chloride may be obtained without any oxide either by direct union of magnesium and chlorine or by preparing a double salt $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl}$. This may be obtained by heating a mixed solution of magnesium chloride and ammonium chloride until the double chloride crystallises out. On heating this, ammonium chloride is driven off and anhydrous magnesium chloride remains.

198. Hydrochloric acid does not attack the so-called "noble metals", platinum and gold. These metals, however, dissolve in aqua regia, which is a mixture of about three parts by volume of concentrated hydrochloric acid with one of nitric. Aqua regia is a powerful oxidising agent.

199. Bromine and iodine form similar acids, but these acids cannot be prepared by the method used for hydrochloric acid. If a bromide or iodide be treated with sulphuric acid, the haloid

acid evolved partly decomposes and free bromine or iodine is liberated, the hydrogen produced acting upon the sulphuric acid and reducing it to sulphur dioxide or even to sulphuretted hydrogen, H_2S . In the case of an iodide the latter is produced in sufficient quantities to be detected by its smell. In the case of both bromide and iodide a piece of lead acetate paper is blackened when held over a test-tube in which the action is taking place. This is a test for H_2S (see § 369).

200. The acids are produced by the action of the halogen on red phosphorus in the presence of water. When dry, the elements combine with phosphorus to form the bromide, PBr_3 , and the iodide, PI_3 . In presence of water these decompose thus:



The apparatus is shown in fig. 25. The U-tube contains dry red phosphorus to absorb any bromine carried over, and is not required when preparing HI .

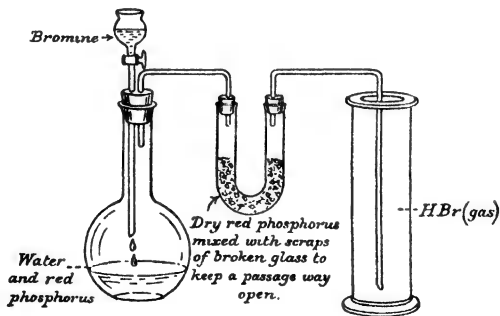


Fig. 25. Preparation of Hydrogen Bromide.

When preparing hydrobromic acid, the bromine is conveniently placed in the dropping funnel, red phosphorus and water being in the flask. For hydriodic acid the water is in the funnel and the phosphorus and iodine in the flask. The liquid in

the funnel is dropped in gradually, as the action is somewhat brisk.

201. Fluorine, the fourth member of the family, is an element the reader is not likely to meet with in a free state. The element is the most active of all the non-metals and readily attacks almost anything, including glass. Seeing that chemical apparatus is made of glass, the difficulty this raises will easily be realised. It was originally prepared by Moissan (1886) by the electrolysis of hydrofluoric acid containing potassium fluoride in solution. The apparatus used by Moissan consisted of a platinum-iridium U-tube and electrodes with fluor-spar stoppers, the whole being cooled by immersion in methyl chloride, a liquid which boils at -23°C . The apparatus is shown in fig. 26.

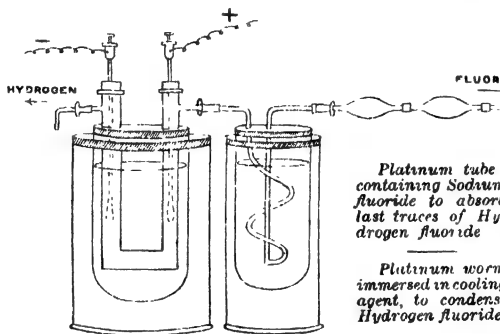


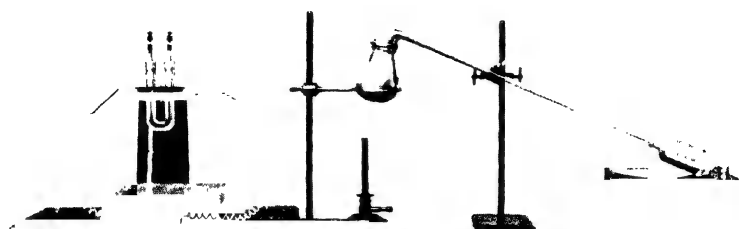
Fig. 26. (See also Plate IV.)

Fluorine has since been successfully obtained by using a U-tube of platinum and even of copper. In this case the copper is attacked, but a layer of copper fluoride is formed which prevents the action going further. The electrodes, however, are always of platinum-iridium.

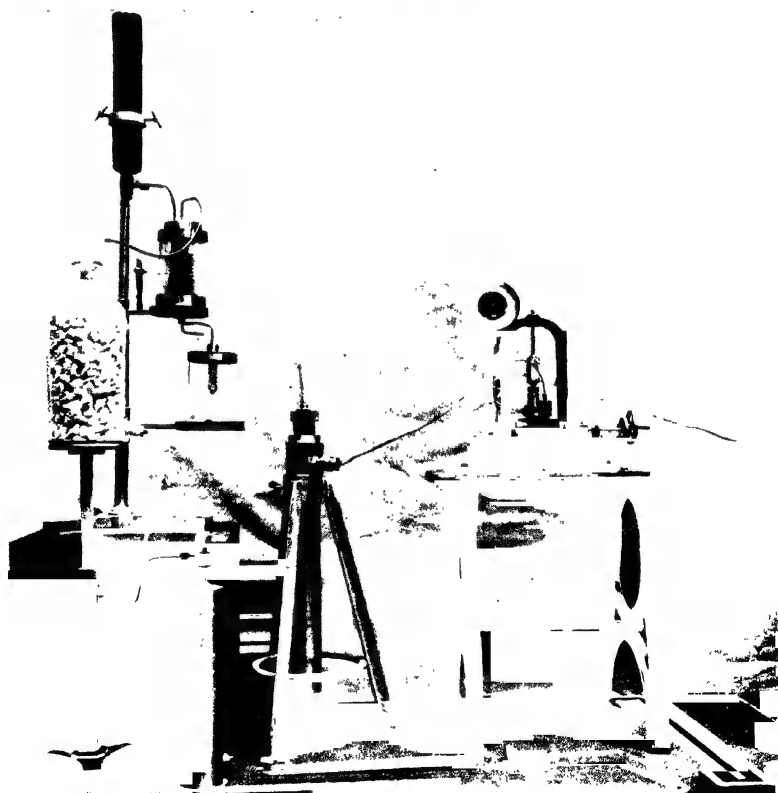
202. Fluorine is a yellow gas lighter in colour than chlorine. Its atomic weight is 19 and its molecular weight 38, so the



Manufacture of Hydrochloric Acid
by burning hydrogen at silica burners (inside the wire guards) in a current of chlorine.



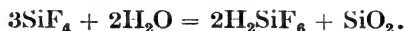
Moissan's Preparation of Fluorine.



The Original Apparatus for Liquefying Oxygen.

molecule is represented by F_2 . It will be noticed that it is a little heavier than air. It attacks water and forms hydrofluoric acid, the energy liberated being partly taken up by the oxygen which is thereby converted into ozone (see § 485).

203. The substance formed when fluorine attacks glass or a silicate is a heavy gas, silicon tetra-fluoride, SiF_4 . This gas readily combines with water thus:



The substances produced are hydrofluosilicic acid in solution and gelatinous silica.

204. Hydrofluoric acid is produced when sulphuric acid and a fluoride are heated together. The acid, like fluorine, attacks glass, so a lead vessel is used. The acid is liquid, but has a very low boiling-point, $19^\circ C$. It is usually stored mixed with water in an india-rubber bottle. It is used for etching glass. A simple experiment will illustrate this. A piece of glass is coated with paraffin wax (in other words, candle grease from a wax candle) and then written on with a dry pen. The writing is then held over the fumes from a bottle of hydrofluoric acid for a minute or so or treated with a solution of the acid, and after the removal of the wax the writing is found to be etched into the glass. In this way the graduations upon thermometers and other apparatus can be marked. This is a common practical use for hydrofluoric acid.

Hydrofluoric acid is so active that it is dangerous to handle. Some of the earlier workers lost their lives while experimenting with the gas and others were seriously disabled.

205. The natural sources of fluorine are the mineral fluor-spar, CaF_2 , and a double fluoride of aluminium and sodium, $AlF_3 \cdot 3NaF$, called cryolite. Apatite is a double salt made up of calcium phosphate and calcium fluoride, $3Ca_3(PO_4)_2 \cdot CaF_2$.

206. At this stage the student will do well to go over the properties of the halogens and compare them. The properties of

bromine are intermediate between those of chlorine and iodine. The atomic weight, 80, is just about the mean of those of chlorine and iodine, 35.5 and 127.

Taking the halogens in the increasing order of their atomic weights—fluorine, chlorine, bromine, iodine—it will be noticed that the melting-points and the boiling-points are in the same order. Also the colour darkens as the atomic weight increases. Their affinity for hydrogen decreases with the atomic weight, and the properties depending upon this affinity vary in the same way. Thus the bleaching action decreases, iodine showing no bleaching action, while that of bromine is less than that of chlorine. The irritating nature of the smell decreases as the atomic weight rises, and this again may be due to the decreased affinity for hydrogen. It is more than likely that the pungent effect of chlorine on the mucous membrane is due to combination of the gas with hydrogen. The solubility in water also decreases as the atomic weight rises.

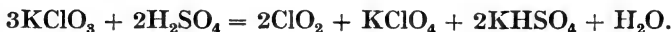
207. Antimony, arsenic and phosphorus all combine directly with the halogens as do many metals, forming chlorides, bromides, etc. It is interesting to note certain similarities between the "halides" of metals. They are for the most part soluble in water. The chloride, bromide and iodide of lead are all only slightly soluble in cold water, but readily dissolve in hot. Lead chloride is white and the other two yellow. Mercuric iodide is insoluble in water, the bromide and chloride are both somewhat soluble, especially in hot water. The silver salts of all three are insoluble, and again the chloride is white and the other two yellow. The fluorides, on the other hand, show some marked contrasts to the other halogen compounds. Silver fluoride is very soluble in water and is deliquescent. Calcium chloride is well known as a deliquescent salt. Calcium fluoride, on the other hand, is a hard mineral which appears about as insoluble as glass. The fluorides of mercury are unstable.

208. The compounds of the halogens with oxygen are inter-

esting. No oxides of fluorine or bromine have been definitely identified. Chlorine yields two unstable oxides, chlorine monoxide, Cl_2O , and chlorine dioxide, ClO_2 . The former is prepared by passing dry chlorine over cooled and freshly precipitated mercuric oxide:



The latter can be obtained by the action of strong sulphuric acid upon potassium chlorate:

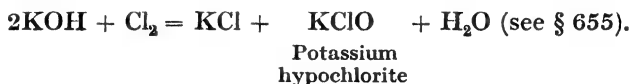


Notice that this is a method of preparing a perchlorate.

Chlorine dioxide is very explosive and the beginner is advised *not* to try this experiment for himself.

Iodine forms at least one oxide, I_2O_5 , which is a white powder, stable at ordinary temperatures but decomposed by heat.

209. When chlorine is passed into a *cold* solution of caustic potash the action is:



Bromine acts similarly.

On passing chlorine into a *hot* solution of caustic potash the action is:



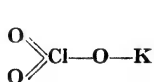
Bromine acts similarly. Iodine acts in this way whether the solution be *hot* or *cold*.

210. By such means hypochlorites and chlorates are formed, also hypobromites and bromates and iodates. Perchlorates (e.g. KClO_4) and per-iodates (e.g. KIO_4) are known, but no per-bromates. Acids corresponding to these salts are known— HClO , HClO_3 , HClO_4 , HBrO , HBrO_3 , HIO_3 , HIO_4 —as are also chlorous acid, HClO_2 and chlorites.

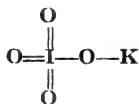
211. If the reader considers these facts carefully he will see

that they agree with the facts already noted, that iodine has the greatest and bromine the least affinity for oxygen of the three halogens chlorine, bromine, and iodine. The affinity for oxygen shows no regular gradation with atomic weight and so is exceptional. No oxy-acids of fluorine are known.

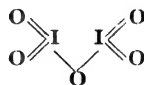
212. In their commonest compounds the halogens are univalent, but not in their oxy-acids and their salts. The valency may be 3, 5 or 7. The following structural formulae illustrate this:



Potassium chlorate



Potassium per-iodate



Iodine pentoxide

213. Chlorine dioxide is anomalous, and should be compared with the corresponding oxide of nitrogen. The latter, however, is stable while the former is not.

Though the halogens are usually univalent, their higher valencies are of great theoretical interest in the more advanced study of the relationships between the elements.

214. By now the reader will have concluded that fluorine is the "odd man out" among the halogens and does not fit any too well into the group. It was long ago remarked that fluorine appears to bear some resemblance to oxygen. This should be borne in mind, as the fact has its place in the scheme of chemical science.

Chapter XVIII

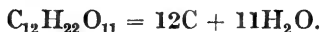
CARBON AND ITS OXIDES

215. Carbon is one of the most widely spread of elements. It is an essential ingredient of all living matter, both animal and vegetable, it occurs in the air as carbon dioxide and it is found in vast quantities in the limestones of the mineral world. It occurs to some extent as the free element. Free carbon is found in nature as **graphite** (the black lead of pencils) and as **diamond**. Much free carbon also occurs in coal. In combination, carbon is found principally in carbonates, chiefly calcium carbonate. As this includes limestone of which the Alps and the Pennine chain are mainly composed, and chalk, which is so abundant in the south and east of England and elsewhere, it will easily be seen that carbon is plentiful enough in the mineral world. Coral reefs consist mainly of limestone, and the evidence shows that the bulk of the limestones in the world are, like coral reefs, the remains of the hard parts of countless marine creatures of the past. Dolomite, which contains the carbonates of calcium and magnesium, and magnesite, mainly magnesium carbonate, are both plentiful, and carbonates of other metals are also found in smaller quantities. Petroleum and other mineral oils, round which such a vast industry has grown up in this age of motor traction and oil fuel, are essentially compounds of carbon and hydrogen, as is also natural illuminating gas.

So the reader will gather that, whatever may be the case with the oil supply, no shortage of carbon is likely to occur. Carbon is so important to life that the amount of life on the earth—both animal and vegetable—is strictly limited by the amount of the element available. Once this fact is grasped it will come as a relief to know—as the poverty-stricken old lady remarked when

first she saw the sea that here, at any rate, is something of which there is enough.

216. The commonest method of producing carbon is to heat organic matter, such as wood or coal (coal being originally of organic origin), in a closed space, i.e. without free access of air. In this way carbon is obtained from wood, as charcoal, or from coal, as coke. These both contain some mineral matter. Bone black, or animal charcoal, produced in the same way from bones, consists of calcium phosphate with a considerable admixture of carbon. As the carbon is present to the extent of only about 10 per cent., it is only by courtesy that it can really be classed as a form of carbon at all, though it is to the carbon present that it owes its distinctive properties (see § 223). A purer form of carbon is ordinary chimney soot. Purer still is "lamp-black" formed by burning almost any hydrocarbon (see chap. XIX) and holding a cold surface in the flame. A very pure form of carbon is obtained by charring sugar. Sugar is a compound of carbon, hydrogen and oxygen, the two latter being in the same proportions as they occur in water. On heating without a supply of air water is driven off:



The reason why this produces such pure carbon is that the sugar itself can, by crystallisation, be thoroughly purified. Strong sulphuric acid removes water from sugar and leaves carbon, in the same way (compare with § 242).

217. These methods all yield **amorphous carbon**, that is, carbon without any definite crystalline form. The two naturally occurring crystalline forms of free carbon already mentioned can be produced artificially. Carbon is insoluble in nearly every known liquid. It will dissolve in molten iron. From such a solution on cooling some of the carbon is recovered as graphite, which, however, is best made artificially by heating coke and sand in an electric furnace, and this process is used industrially.

Large quantities are now made by this process in America, the power being derived from the Niagara Falls. Graphite also occurs naturally in Siberia, Ceylon and the United States.

218. The artificial manufacture of diamonds has never been achieved on a commercial scale. Moissan (1896) claimed to have produced small diamonds mixed with graphite. He dissolved carbon in molten iron and dropped the solution into molten lead. This cooled the outside and solidified it. The inside cooled later, and as molten iron expands on solidifying, the inside cooled under great pressure. When the iron was dissolved away by acid, he found what he thought were small diamonds in the residuc, together with particles of graphite. Recent research has failed to confirm this.

219. When an element exists in more than one distinct form the different kinds are called **allotropic** modifications. These different modifications no doubt depend upon some difference of molecular structure.

Carbon, then, exists in at least three allotropic forms, two crystalline—diamond and graphite—and at least one amorphous. Amorphous carbon from different sources, e.g. charcoal and gas carbon, differ so much that it would perhaps be fair to call them separate allotropic forms. But here the difference may be due to impurities combined with the carbon, and not be merely a difference of form.

The fact that the different kinds of carbon actually consist of carbon, and of nothing more, may be shown by burning in oxygen a weighed quantity of each. On burning, the substance formed is the heavy gas carbon dioxide, which readily combines with caustic soda. So the carbon dioxide formed can be absorbed and weighed, and it is found that equal weights of the three forms of carbon give equal weights of carbon dioxide and nothing else.

220. All three forms of carbon have their uses. Diamond, the most ornamental of the three forms, is quite the least useful. But

besides its use as a gem, it is an excellent polishing and cutting material, being exceedingly hard. Carbonado, a black substance, often found along with diamonds, consisting of a less pure form of carbon, is harder even than diamond. It is used for diamond polishing and for glass cutting.

221. Graphite, besides being used in pencils, is the basis of the familiar "black lead" used to shine stoves. It is also used instead of oil to act as a lubricant. It is a good conductor of electricity (which diamond is not), and so can be used to coat bodies which are not themselves conductors, to prepare them for electro-plating.

Both diamond and graphite are very permanent substances. Practically no reagents act upon either of them under any ordinary conditions. Hence graphite is of use for making crucibles. Diamond is, of course, too expensive to be of any great practical use.

222. Amorphous carbon is used as a fuel as **charcoal** and as **coke**. Powdered charcoal is an ingredient of gunpowder. Wood charcoal has the remarkable power of absorbing gases. For example, if a tube of ammonia gas be inverted over mercury and a piece of charcoal introduced, the gas is absorbed and the mercury rises in the tube. This power of absorbing gases promotes chemical action between them. The gases are packed closely together in the pores of the carbon. This property makes charcoal useful as a disinfectant, especially in absorbing gases with bad odours. Sulphuretted hydrogen, for example, is absorbed and oxidised by charcoal in the presence of air. To show to the full this absorbent property, the charcoal should first of all be placed in the receiver of an air-pump and the gases it has already absorbed removed. Coco-nut charcoal, cooled in liquid air or liquid nitrogen, is very effective in absorbing gases. It is used in this way to produce very high vacua. The absorbent power of charcoal decreases with rise of temperature.

223. Lamp-black or soot is used as a black colouring matter,

as, for example, in printing-ink and in boot-blackening. For especially high-class productions the carbon is obtained by dehydrating sugar (see § 216).

Bone-black, or animal charcoal, has the remarkable property of removing the colouring matter from many organic substances in solution. The solution is passed through a filter containing the bone-black and comes out colourless. In this way white sugar is made from brown.

Carbon is of no use as a manure. Soot, however, is frequently used for this purpose. The carbon in the soot remains in the field unchanged; it is the ammonium salts present as an admixture which make the soot useful as a plant food.

224. Chemically, carbon is at ordinary temperatures inert. It will burn in oxygen or in contact with any substance which readily parts with oxygen. It is used in industry to obtain metals such as iron or copper from their ores, but these reactions require high temperatures—some of them very high temperatures. The ordinary fluid reagents of the laboratory do not act upon carbon in any form below their boiling-points.

225. Carbon as powdered charcoal is used as a medicine, either just as it is or made up with flour into biscuits. These biscuits are black, but in spite of their terrifying appearance are not bad eating. The effect depends upon the carbon absorbing gases produced by fermentation in cases of dyspepsia, and the more distressing symptoms of even far more serious diseases can sometimes be eased in this way.

226. The atomic weight of carbon is 12, and the valency in all its compounds—with one solitary exception, carbon monoxide—is always four.

227. Chemistry is full of surprises, and the compounds of carbon certainly contribute their fair share. The number of compounds of carbon is legion, and they have been given a whole subdivision of chemistry to themselves—**Organic chemistry**. It is called “organic” because it was the presence of these compounds

in living organisms, both plants and animals, that first drew attention to so many of them, and it was thought that they could only be produced by the activities of living things. This is still true of many of them, though the number which has been produced by purely chemical means increases almost daily. Many thousands of compounds of carbon are known. They include all kinds of food-stuffs—sugars, starch, fats, proteins, etc.—the derivatives of coal, including naphthalene, light and heavy oils, benzene, toluene and the explosives derived from it, aniline and the dyes derived therefrom; also saccharine and many drugs. Cellulose, a very important compound of carbon, forms the basis of wood, paper, linen, cotton, artificial silk and a number of other substances. But a mere list of the compounds of carbon would make a large book of itself. There can surely be no more astonishing fact in nature than this—that food-stuffs such as starch and sugar, violent poisons like prussic acid and strychnine, beautiful dyes like alizarine and rosaniline, and matter-of-fact substances like xylonite and cellulose can all be resolved into a black powder, carbon, together with three at most of the colourless, odourless and somewhat tenuous gases, oxygen, hydrogen and nitrogen.

For the moment we will just consider the two oxides of carbon and a few of its compounds with hydrogen.

228. Carbon dioxide, CO_2 , is a heavy gas, formed when carbon is burnt with plenty of oxygen. Its density ($H = 1$) is 22, as the reader should be able to deduce at once from the formula (but see § 120). It is readily produced by acting upon almost any carbonate with any but the very feeblest acids. It can easily be made in the kitchen by dissolving washing soda, which is sodium carbonate, in lemon juice or in vinegar. For example, vinegar contains acetic acid and the action is:



In the laboratory it is usually made from limestone, marble or

chalk (which are all forms of calcium carbonate) and hydrochloric acid:



(see § 657). The formula CO_2 is justified in § 658.

The gas is a little soluble in water, yielding the very feeble acid, carbonic acid, H_2CO_3 . It is, however, not so soluble that it cannot be collected over water. Being heavy it can be collected by passing it downwards into a jar of air and allowing it to displace the air upward.

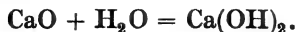
229. The carbonates of sodium and potassium— Na_2CO_3 , K_2CO_3 —are not decomposed by heat, but most other carbonates give off carbon dioxide when strongly heated. This provides a common and simple way of preparing oxides. For example, chalk* is used in this way to prepare quicklime, CaO :



230. Quicklime is a substance of considerable practical importance. It is produced in a special kind of furnace called a "*lime-kiln*". The calcium carbonate is mixed with coke or coal and made to burn in the furnace, the combustion keeping up a current of air through the mass. The waste gases— CO_2 and nitrogen, with possibly a little CO —escape at the top and the lime remains in the kiln as a white powder. By introducing the coke and carbonate at the top the lime can be removed from time to time in a sufficiently pure state at the bottom, since by the time the charge has reached the lower part of the kiln the coke is practically all burnt away. The kiln is kept continually operating day and night. It requires little attention beyond keeping up the supply of fresh materials at the top. The action of heat on carbonates should be compared with the action of heat on nitrates (see § 301).

* The prepared chalk sold for writing on blackboards does not usually consist of calcium carbonate.

Quicklime when mixed with water gets very hot and forms slaked lime, $\text{Ca}(\text{OH})_2$:



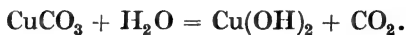
This action is attended with an increase in bulk, i.e. the slaked lime occupies more space than the quicklime from which it is made. This expansion has a real practical use. If cartridges made of quicklime are placed in borings in rocks, the expansion when they are moistened is so great that it may be made to split the rock. This method is used in mining and is clearly safer than the use of an explosive. Slaked lime is used for the preparation of mortar.

Slaked lime is slightly soluble in water, yielding a feebly alkaline solution of calcium hydroxide or lime water.

231. When a carbonate is produced by double decomposition it usually breaks up partly into the hydroxide and carbon dioxide, the latter being given off. For example, if solutions of copper sulphate and sodium carbonate are mixed the action is:



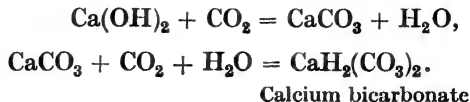
and some of the copper carbonate immediately decomposes thus:



The ultimate result is a mixture of the carbonate and hydroxide of copper, the exact composition depending on the temperature, the strengths of the solutions, etc. The carbonates of calcium, barium and strontium do not decompose in this way. On the other hand, those of aluminium and ferric iron are practically completely decomposed. The action which takes place when solutions of a soluble carbonate and of a copper salt are mixed is a striking one and can hardly fail to interest and surprise anyone who sees it for the first time.

232. The simplest test for carbon dioxide is to pass it into a solution of lime water, already described. A white precipitate is

produced, and this phenomenon has from time immemorial been described in text-books and lectures by saying that the lime water "turns milky." This milkiness clears up on passing further carbon dioxide into the lime water, owing to the formation of the more soluble bicarbonate:



The bicarbonate is decomposed on boiling and the carbonate again precipitated.

233. The presence of salts of calcium or magnesium in solution in water causes what is known as **hardness**. Hard water does not easily give a lather with soap. Why this is so may be seen by considering briefly what soap is. Many animal and vegetable fats contain, among other things, compounds of various somewhat complicated organic acids. What exactly these acids are does not at present matter. Let us suppose such an acid can be written HX , where X stands for the organic radicle of the acid. There are several different acid radicles of this kind in soap. X will serve for our immediate purpose to stand for any one of them. Soap is a sodium salt (or more rarely a potassium salt) of such an acid and so may be written NaX . Now suppose soap is dissolved in water containing calcium bicarbonate in solution. A chemical action—a double decomposition (see § 145)—takes place thus:



CaX_2 is an insoluble substance, which forms the curdy precipitate often seen on the surface of soapy water. Or, again, if the water contains calcium sulphate in solution the action of soap is



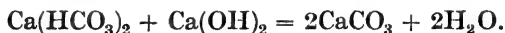
In either case there is a waste of soap, as all the calcium must be precipitated before any soap solution can be prepared. Hardness

is thus a real disadvantage in the ordinary process of washing. It may be *temporary* or *permanent*. Hardness is said to be "temporary" if it is removed simply by boiling. This is the case when the salt causing the hardness is a bicarbonate, bicarbonates being decomposed by heating the solution up to boiling-point:



Hardness due to the presence of other salts, such as sulphates or chlorides of calcium or magnesium, cannot be removed merely by boiling and is called "permanent" hardness. It is only relatively permanent as, though not removable by boiling, it can be removed easily enough in other ways. Hence the paradox involved in the common question "How can permanent hardness be removed?" need cause no surprise.

234. Removal of hardness. Temporary hardness can be removed as above, by boiling, or by addition of the right quantity of lime. In the latter case the equation is

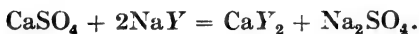
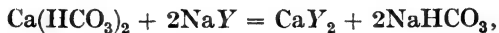


This process is only possible if the quantities are carefully chosen. An inspection of the equation will show that the weight of calcium introduced must equal the weight already present. The water must be analysed to find out how much this is, before the lime is added, for if the quantity added be too big the excess will make the water hard again. To be sure he understands this the reader should satisfy himself that if the right quantity of lime is added all the hardness is corrected, if *twice* the right quantity the water will be just as hard as it was originally, and if more than twice, the water will be harder than ever.

235. Let us now consider the removal of "permanent" hardness. We have already seen that this is removed by soap. It could, of course, also be removed by distillation, but this is far too drastic and expensive a process for general use. Distilled water is, however, beautifully soft as also is rain water.

Sodium carbonate will remove permanent hardness, but the

removal of hardness, temporary or permanent, is now best effected by a process known as the "permutite" process. "Permutite" as used for this purpose is a substance like coarse sand. It is a sodium salt of a somewhat complicated kind, containing both silicon and aluminium—"sodium aluminium silicate" or "sodium silico-aluminate." In order to understand its use an exact knowledge of its composition is unnecessary. Let us write it NaY . Its action on the calcium salts in hard water may be written:



The permutite is changed into a new substance CaY_2 , still insoluble. But the particular charm of the process is this. If CaY_2 is immersed in a solution of ordinary salt, the permutite is restored according to the equation:



The permutite is washed and the CaCl_2 thrown away. The only material actually used up is the salt, which is very cheap. A given charge of permutite spends part of its time softening water, the water being run through it as through a filter. It is regenerated, that is, changed back into the sodium salt, by being immersed in brine (i.e. salt solution). The recovery is practically complete and the same charge may remain in use for years.

236. The water in a district is "hard" or "soft" according to the nature of the land around. On any chalky soil or in any limestone district, for example, the water is hard. The "fur" which collects in kettles and boilers is due to these calcium salts, which in some industrial processes constitute a very considerable nuisance. An excess of lime in drinking water is harmful to people who are liable to suffer from gout. Hence the real usefulness of such a process as the permutite process will be obvious.

Hard water is generally less pleasant to the hands than soft

water. Anyone living in a hard-water district knows the added pleasure in washing when he happens to find himself in a district where the water is soft. In shaving—as the reader may or may not have discovered—the difference is even more marked.

237. Carbon dioxide combines readily with alkalis, yielding carbonates: $2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}.$

Sodium carbonate

The gas in many natural waters and in artificial waters such as soda water and also in effervescent or sparkling wines is carbon dioxide. It is a gas dangerous to life, not because it is poisonous but because it displaces the air, and owing to its heaviness it collects in hollows and does not readily diffuse away. For example, much carbon dioxide is produced in brewing and it can easily happen that an incautious man is suffocated by the air over a brewing vat. The perils of strong drink start at the very source.

238. The air in mines after an explosion contains much carbon dioxide instead of oxygen. This spent air is known to the miner as *choke-damp*. When venturing into a well or other closed space where the atmosphere may perhaps consist mainly of carbon dioxide a lighted candle is commonly introduced first. If it burns without difficulty, it may be considered safe to proceed. Or a bird or mouse may be used for the purpose. If the creature falls senseless it has given its warning, and if at once withdrawn recovers and is none the worse. There is at least one place in Italy visited by tourists where there is naturally occurring carbon dioxide and where a dog is kept specially for the interest of visitors. This dog goes through the process of temporary asphyxia daily.

239. Carbon dioxide does not usually support combustion. Magnesium ribbon, however, will burn in it and a fine deposit of soot is formed: $2\text{Mg} + \text{CO}_2 = 2\text{MgO} + \text{C}.$

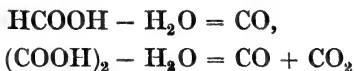
240. Carbon dioxide contains carbon in its “spent” form. Almost all the useful compounds of carbon are on their way to turning into carbon dioxide, yielding up their energy in the

process. This opens the way to one of the most romantic chapters in science, a story which can compete with tales of pirates or detectives for interest. This story must, however, be postponed for the present and will be found in chap. xxiii.

241. Carbon monoxide. Though carbon monoxide and carbon dioxide are in a sense brothers, they are as unlike as brothers often are in real life.

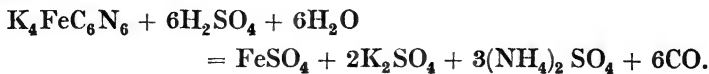
The formula of carbon monoxide is CO, and hence the reader can see for himself that the gas is 14 times as heavy as hydrogen, or about as dense as nitrogen and a trifle less dense than air.

242. Carbon monoxide is formed when carbon is burnt with a poor supply of oxygen or when carbon dioxide is passed over red hot carbon. It is, however, most easily produced by heating strong sulphuric acid with formic or oxalic acid or with a salt of either (see § 659). The sulphuric acid removes the elements which form water:



(compare with § 216). In the second case both oxides of carbon are liberated. Carbon monoxide is not soluble either in water or in alkalis. If therefore the mixed gases be bubbled through caustic soda solution, carbon monoxide comes through alone. Oxalic acid is more used for this purpose than formic acid. True the latter gives a yield of pure gas, but formic acid is very much more expensive.

243. Carbon monoxide is also liberated when potassium ferrocyanide is heated with a large excess of concentrated sulphuric acid:



The potassium ferrocyanide is powdered before adding the acid. This salt crystallises as $\text{K}_4\text{FeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$, and the water of crystallisation with the small amount of water usually found even

in strong commercial sulphuric acid supply the $6\text{H}_2\text{O}$ required by the equation. The presence of CO in "water gas" has been mentioned in § 53.

244. Carbon monoxide is a colourless gas which burns with a hot, light blue flame yielding carbon dioxide, thus:

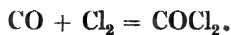


The blue flame seen on the surface of a coal or charcoal fire is due to this cause. The oxygen in the air, passing up through the fire, in presence of excess of carbon, is converted into carbon monoxide, which burns on reaching the air at the top.

Carbon monoxide readily combines with oxygen and is thus a good example of a reducing agent (see §§ 475 and 659). It may be used to effect the *reduction* of a number of compounds, i.e. to extract the oxygen from them. It will be recollected that hydrogen is also a reducing agent. The reducing properties of carbon monoxide play an important part in the smelting of some metals, as will appear later (see § 560).

Carbon monoxide is very poisonous, as explained in § 40. Coal gas contains carbon monoxide; hence its popularity with suicides. Any fire burning with insufficient air may produce carbon monoxide, and mishaps due to such causes occasionally occur. The waste gases from the exhaust of a motor-car contain CO, and fatal accidents due to running the engine in a closed space are not uncommon. If the engine is running in a small garage, the doors *must* be left wide open.

245. The structural formula of carbon monoxide is $\text{C}=\text{O}$. Now carbon is usually not bivalent but quadrivalent, and hence carbon monoxide readily combines with several elements to **saturate** the carbon. For example, if chlorine and carbon monoxide be mixed in equal quantities and exposed to bright sunlight, they combine at once and form **carbonyl chloride** or **phosgene gas**:



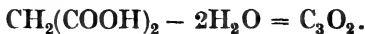
The mixture must be kept cool during the process, as much heat is generated by the action. Carbon monoxide is a good example of an **unsaturated** compound, a phrase the student will meet with a good deal (compare §§ 252, 256, 264).

246. Carbon monoxide also combines directly with certain metals to form compounds called **carbonyls**. Thus with finely divided iron it forms a liquid compound ferropentacarbonyl, $\text{Fe}(\text{CO})_5$, and with nickel, nickel carbonyl, $\text{Ni}(\text{CO})_4$. The formation of the latter can be used in the practical extraction and purification of nickel. The carbonyl is, however, a volatile and very poisonous liquid, and consequently the process is dangerous to work and requires great care.

247. Once the composition of carbon dioxide is known, that of carbon monoxide is easily determined.

A measured volume of carbon monoxide is mixed with a measured volume of oxygen in a eudiometer and the mixture sparked. By absorbing in caustic soda the carbon dioxide from the gases produced, it is found that (1) carbon monoxide when sparked with oxygen yields a volume of carbon dioxide equal to the original volume of carbon monoxide used and (2) uses up half its own volume of oxygen in the process. Thus two molecules of carbon monoxide combine with one molecule of oxygen to produce two molecules of carbon dioxide; or a molecule of carbon dioxide (whose formula is known to be CO_2) is formed from a molecule of carbon monoxide and half a molecule (i.e. one atom) of oxygen. In this way the formula CO is justified. The equation is seen

In addition to carbon dioxide and carbon monoxide there are some other oxides of carbon, the chief of which is carbon suboxide C_3O_2 . This compound is obtained by the action of dehydrating agents on malonic acid:



Malonic acid

Chapter XIX

THE SIMPLER HYDROCARBONS

248. The **hydrocarbons**, compounds of carbon and hydrogen with each other and with nothing else, are very numerous. Several familiar substances—acetylene, paraffin wax, vaseline, the bulk of the mineral oils, petrol, benzene and some others—are either hydrocarbons or mixtures of hydrocarbons.

249. They will be most readily understood if we remember that carbon is quadrivalent and hydrogen univalent. This at once suggests a possible hydrocarbon CH_4 , which is in fact *marsh gas*. Suppose we imagine one atom of hydrogen removed. The

residue may be written $\text{CH}_3\text{—}$ or $\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—}$. This is not the formula

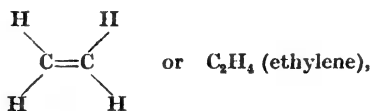
of a *substance* at all. The carbon has a fourth valency unsatisfied. But the group, $\text{CH}_3\text{—}$, can be treated much as a univalent element, and thinking of it in this way, it might form a chloride CH_3Cl , a hydroxide CH_3OH or an oxide $(\text{CH}_3)_2\text{O}$. These substances do actually exist. They are called methyl chloride, methyl alcohol and methyl oxide (or, better, methyl ether) respectively. $\text{CH}_3\text{—}$ is a **compound radical** and is referred to as **methyl**. Notice quite definitely that it is not a free substance; it is a group of atoms which occurs in many compounds and can conveniently be thought of as a whole. It should be recollected that *atoms* of elements such as hydrogen do not normally exist in the free state. Suppose, then, we remove one of the atoms of hydrogen from CH_4 and insert the univalent radicle $\text{CH}_3\text{—}$ in its place. We get $\text{CH}_3\text{—CH}_3$ or C_2H_6 . Replace another H and

we get C_3H_8 , another and we get C_4H_{10} . In this way we get a "homologous" series:

CH_4 ,	Marsh gas or methane.
C_2H_6 ,	Ethane.
C_3H_8 ,	Propane.
C_4H_{10} ,	Butane.
C_5H_{12} ,	Pentane.

By building up in this fashion, the formulae of a large series of compounds can be written down, members of which are actually known at least up to $C_{35}H_{72}$. It will be noticed that the general formula for members of this series is C_nH_{2n+2} . These hydrocarbons are known as *paraffins*. It is the extraordinary power which the carbon atoms have of linking themselves up together in compounds which makes organic chemistry such a vast field.

250. But this is only the beginning of the story. There are other homologous series of hydrocarbons. One of these begins with *ethylene* and another with *acetylene*. To these the following formulae are assigned:



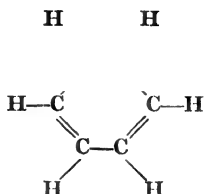
and



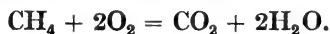
These are the starting members of two more homologous series whose general formulae are C_nH_{2n} and C_nH_{2n-2} respectively. We have only to take away an atom of hydrogen and replace it by CH_3 and continue as before.

The matter is rendered still more complicated and more interesting by the existence of cyclic compounds, in which the last carbon of a series is joined to the first to form a ring. An

important compound of this type is **benzene** C_6H_6 , which has the formula



251. Marsh gas or Methane. We shall only have space for the present to discuss the very simplest of these compounds. We shall start with marsh gas, CH_4 . This is a light gas, insoluble in water and which burns readily in air:



It is produced by heating sodium acetate with caustic soda in a hard glass tube:



The gas comes off easily and at a lower temperature if soda lime (which consists of the hydroxides of both calcium and sodium) is used instead of caustic soda.

This is an example of a method by which a number of hydrocarbons can be made from the sodium salt of the appropriate organic acid. Thus, sodium propionate, C_2H_5COONa , yields C_2H_6 , ethane, when heated with soda lime. Compare this action with the method given for preparing hydrogen from a formate (§ 54). Similarly benzene, C_6H_6 , can be made from benzoic acid or from sodium benzoate:



252. Methane is a saturated hydrocarbon, i.e. all four valencies of the carbon are fully occupied. This is shown by the fact that it forms no addition compounds, or in other words it does not combine with other substances. It does, however, form replacement or substitution compounds. Thus, with chlorine,

CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 , together with hydrochloric acid, are all easily and directly formed. Of these, CHCl_3 is well known as chloroform. The anaesthetic properties of this remarkable substance were discovered by the German chemist Liebig (1832) and popularised in this country by Sir James Simpson (1847). These men by the discovery of anaesthetics and Lord Lister by the introduction of antiseptic surgery have done far more to promote human welfare than soldiers or statesmen can ever hope to do. The student of science will do well to remember

“How small, of all that human hearts endure,

That part which laws or kings can cause or cure.”*

“The pen is mightier than the sword”†; the test-tube is mightier than either.

253. Methane is produced when vegetable matter decays under water. The bubbles which can often be stirred up in a pond consist largely of methane, hence the name “marsh gas”. Coal gas, in addition to free hydrogen, contains much methane, and so does the atmosphere in a badly ventilated coal mine. This ingredient, called by miners “fire-damp”, makes an inflammable mixture with the air and is mainly responsible for explosions in mines. For this reason a naked flame is never allowed. The miner’s lamp, the Davy Lamp, has the flame screened with a close wire gauze. It is found that a flame thus protected has no power of igniting gases outside the gauze. The cooling effect of this gauze shield prevents a flame passing through it. The reader may easily try this for himself. If a Bunsen burner be lit under a horizontal piece of wire gauze (copper gauze is best), the flame does not pass through it. Also if the gas be lighted above the gauze only, it does not travel back to the burner (see figs. 27, 28).



Fig. 27. Davy Lamp.

* Johnson.

† Bulwer Lytton.

In some parts of Canada and the United States towns are lit by a naturally occurring mineral gas, which consists largely of

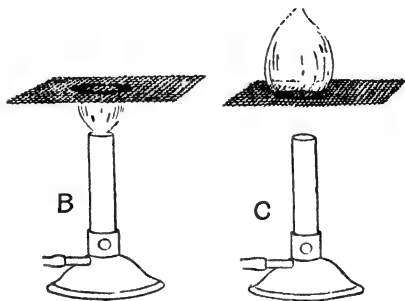
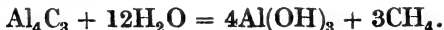


Fig. 28. Conduction of heat by wire gauze.

methane. It is surprising and disappointing to learn, however, that in at any rate one such town (Little Rock, Arkansas) gas bills are not lower than elsewhere.

254. There are a number of compounds known as **carbides**, which are compounds of various elements, chiefly metals, with carbon. These can frequently be regarded as substances in which a metal has replaced the hydrogen of a simple hydrocarbon, much as a metal can replace the hydrogen of an acid. When such a carbide acts upon water it is usual for the hydrocarbon to be liberated. Methane can in this way be obtained by the action of water upon aluminium carbide thus:



255. Ethylene, C_2H_4 , may be made by removing water from ordinary alcohol, according to the equation

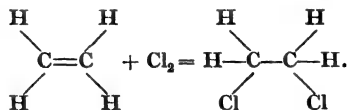


The water is removed by the action of concentrated sulphuric acid. The acid is put in a round-bottomed flask. Alcohol is then added to the extent of about one-third of the volume of sulphuric acid. If the alcohol is in excess, the action produced is

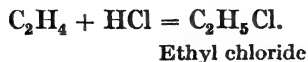
quite different; to produce ethylene the proportions mentioned must be roughly kept to. Ethylene is evolved on moderately heating, and may be collected over water. The gas can also be produced by the action of a strong solution of caustic potash in alcohol on ethyl iodide. The latter is obtained when one hydrogen atom in the molecule of ethane (see § 249) is replaced by iodine. Ethyl chloride or bromide may be used. The iodide is a little more convenient to handle:



256. Ethylene is a colourless gas, of the same density as carbon monoxide. It burns when ignited in air and the flame is smokier and more luminous than that of marsh gas. Chemically marsh gas and ethylene are very different. We have seen that the former does not form addition compounds. The carbon is saturated and only replacement compounds are formed; that is, some hydrogen must be removed before anything else can be introduced into the molecule. But in the case of ethylene the carbon is unsaturated. This is shown by the fact that, on mixing, chlorine and ethylene combine directly in equal proportions without producing any hydrogen chloride. This is explained by the equation:



A similar reaction occurs when ethylene is passed into bromine. Again, with hydrochloric acid the action is:



257. Whenever we have reason to believe that a carbon compound contains a double link, as in the structural formula of ethylene, there is always a possibility of direct combination of a molecule of the compound with two univalent atoms (or groups)

or one bivalent one. Note that a double linkage does not mean that the carbon atoms are more securely fixed together or that the compound is the more stable for the double link. Rather the reverse. Saturated compounds, although containing no double links, are the more stable class.

258. Ethylene is the first member of a homologous series called the *olefines*, $C_n H_{2n}$, each member of which contains two hydrogen atoms per molecule less than corresponding members of the paraffin series (see § 249).

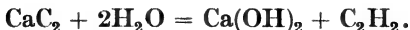
259. Ethylene exists in coal gas, usually to the extent of about 5 per cent. It does not combine directly with hydrogen as easily as it does with chlorine. It will, however, combine directly with hydrogen if a mixture of the two gases be passed over finely divided nickel or platinum.

260. **Acetylene** is familiar as the gas which was formerly so much used as an illuminant for cycles and motor-cars. The formula is C_2H_2 or



It is a colourless gas, a little lighter than air and not very soluble in water. Water will dissolve its own volume of the gas, which, however, is much more soluble in acetone. The reader may think he knows the smell of acetylene. Pure acetylene, however, smells like stale onions; the familiar smell is due to impurities and is nothing like that of the pure gas.

261. For practical purposes acetylene is prepared by the action of water upon calcium carbide:



Contrast this with the action of water upon aluminium carbide (§ 254). Calcium carbide is made from lime and coke by fusing them together in an electric furnace.

262. Acetylene can be prepared by an electric spark discharge in an atmosphere of hydrogen, using carbon electrodes. The union is accompanied with a great absorption of energy (see § 314);

when acetylene burns this energy is liberated, which accounts for the intense light and great heat of the acetylene flame. Use is made of this in oxyacetylene welding. Oxygen and acetylene are burnt together as are oxygen and hydrogen in limelight (see § 39), and the flame is so hot that it can be used to soften and melt metals, even those with high melting-points. For use in this way acetylene is sold as a strong solution in acetone. Liquid acetylene cannot be used, as under pressure acetylene becomes dangerously explosive.

263. Acetylene can also be obtained by the action of a strong solution of caustic potash in alcohol on ethylene bromide, $C_2H_4Br_2$:



Compare this with the similar method given for preparing ethylene. In both cases the strong alkali, caustic potash, may be regarded as being always ready to combine with an acid. This tendency is so strong that it enables it forcibly to remove the elements of the halogen acid and to combine with the acid so formed.

The reaction may be written thus:



and the similar reaction for producing ethylene



The hydrobromic acid of course at once combines with the potash which we have supposed responsible for its removal. In the further study of organic chemistry this use of strong potash will be met with again.

264. Like ethylene, acetylene readily forms additive compounds and is therefore regarded as an unsaturated compound. For example, it combines explosively with chlorine, the action being as expressed by the equation



Acetylene tetrachloride is a liquid which boils at 147°C . and which is non-inflammable. It is used as a solvent. It can be prepared non-explosively by passing the gases acetylene and chlorine into *kieselguhr*, a porous earth. The formula of acetylene given in § 260 expresses its unsaturated nature.

265. Acetylene is the first member of another homologous series C_2H_2 , C_3H_4 (allylene), C_4H_6 (crotonylene), etc.

Chapter XX

DIFFUSION OF GASES

266. If the gas be left on, the smell of gas soon becomes perceptible all over the room, even if the gas jet be well above the level of the nose. There is something to think about here. Coal gas is much lighter than air. An air-balloon filled with coal gas will go at once up to the ceiling and stop there. How, then, does it happen that escaping gas comes down to the level of the nose? If a jar of hydrogen be left open with the mouth upwards and a jar of carbon dioxide with the mouth downwards, the gases immediately escape. This is what would be expected, since hydrogen is lighter and carbon dioxide heavier than air. But if the jars are reversed, the same thing happens though more slowly. If a jar of hydrogen, for instance, is inverted in air, the hydrogen escapes. So also carbon dioxide will escape from a jar of the gas if it is open to the air even with the mouth upwards. Suppose, again, two similar jars containing marsh gas (CH_4) and hydrogen are placed mouth downwards and open to the air. Both these gases are lighter than the air and both escape. But the curious fact is that the lighter gas, hydrogen, escapes more quickly than the less light. This power a gas has of making its way into the space occupied by another gas and mixing with it, even against gravity, is called **diffusion**. It should be noted that once two gases are mixed, however different their densities may be, they will not separate by their difference in weight but remain mixed. If this were not so, the carbon dioxide in the air would form a thin layer near the earth, with another thin layer of argon over it, followed by a thick layer of oxygen and one of nitrogen above that. All gases are completely miscible, which, of course, is not true of all liquids.

267. Experiments to illustrate the diffusion of gases can conveniently be performed by the aid of a sheet of any porous substance which allows gases to pass through it. Compressed graphite is very good for this purpose, but the most easily obtainable is unglazed earthenware. Here is an example. *A* is a jar of unglazed earthenware connected up to a two-necked bottle by tubes as shown in the diagram. *A* and *B* contain air. *C* is water. If now a jar of hydrogen is placed over *A* (as in fig. 29), the hydrogen passes into *A* and air in *A* passes out into

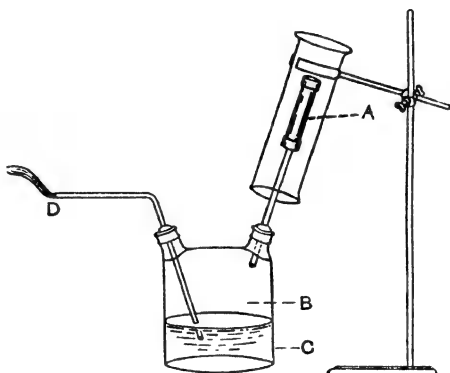


Fig. 29. Diffusion of Hydrogen.

the hydrogen. But the hydrogen is far more diffusible than the air. Hence the number of molecules of gas in *A* increases, the pressure in *A* and *B* rises and a jet of water is forced out at *D*. This is a striking and interesting experiment. Coal gas can be used instead of hydrogen and this has been made the basis of a method of detecting the presence of fire-damp (see chap. XIX) in coal mines. *A* leads to a U-tube of mercury instead of to a bottle of water. The rise of pressure in *A* forces the mercury round the U-tube and can be made to connect up an electric circuit and ring an alarm bell (see fig. 30).

268. If the mixed gases produced by the electrolysis of water

be passed through a tube of unglazed earthenware, such as a clay tobacco pipe, so much more hydrogen escapes than oxygen that the gas issuing from the end of the pipe is not explosive and will

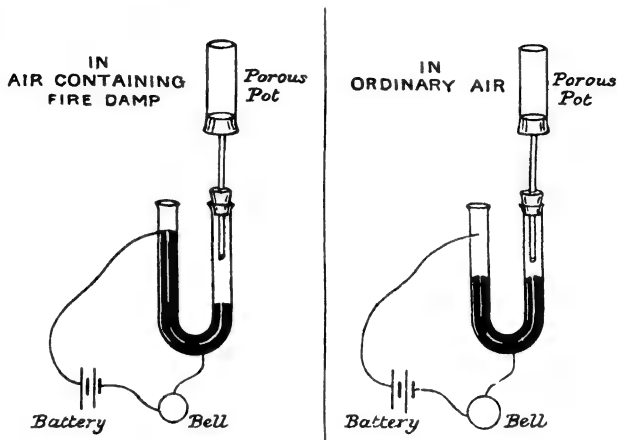
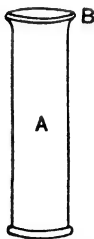


Fig. 30. Diffusion of Hydrogen.

relight a glowing splinter. Note that in all these experiments the unglazed earthenware must be kept dry. Moisture stops up the pores and prevents diffusion (compare this with § 420).

269. The above experiments are for the most part qualitative; that is, they show that diffusion takes place and that light gases diffuse more readily than heavy ones, but they do not give accurate numerical results. For quantitative work a glass tube, *A*, is closed at *B* with a thin sheet of some suitable porous material (fig. 31). Graham, who first investigated these phenomena,



used dry gypsum such as is used for plaster of Paris moulds. This stopper must be thin. If it is not, the thickness introduces a new complication which quite alters the whole experiment. *B* is covered with an india-rubber

Fig. 31. Diffusion of gases.

cap and *A* is filled with mercury. The lower end of the tube is open and stands in a trough of mercury and the tube is then ready for the introduction of the gas to be investigated. *A* can, for example, be filled with hydrogen. The cap is removed from *B* and diffusion takes place. The volume in *A* is seen to contract and after a time the cap on *B* is replaced and the gas in *A* analysed. Thus the amount of hydrogen which is lost from *A* is detected and also the amount of air which has entered. In this way Graham's Law of gaseous diffusion can be verified, namely, that *gases diffuse at rates inversely proportional to the square roots of their densities*.

For example, the density of air is 14.4 and of hydrogen 1. If then 5 c.c. of hydrogen has escaped, how much air has entered? If *x* c.c. of air is the answer, then by Graham's Law:

$$\frac{x}{5} = \frac{\sqrt{1}}{\sqrt{14.4}} \quad \text{or} \quad x = \frac{5}{\sqrt{14.4}} = 1.3 \text{ c.c.}$$

270. For an elementary examination the reader need not know much more about diffusion than has been told him above. But if he is curious to get some idea as to how the phenomenon actually takes place let him read on.

The clue to understanding the matter lies in the theory of gases discussed in § 59 and onwards. A gas is supposed to consist of separate particles, molecules, in rapid motion. At the open mouth of a jar of hydrogen there are molecules of air—or rather of oxygen and nitrogen—in brisk movement just outside, and molecules of hydrogen in brisk movement just inside. It is this movement which causes them to mix. To see why the lighter gas diffuses more quickly than the heavier one, let us digress for a moment.

271. Suppose a large number of people are throwing tennis balls at a wall. Suppose, too, that they throw so many and so frequently that the bombardment amounts almost to a steady pressure on the wall. Now what does this pressure depend on?

Clearly it depends on three things. First, it depends on the mass (or weight, if you like; see chap. 1) of each tennis ball. We will assume the balls are all alike. Second, it depends upon how fast each ball is moving when it hits the wall. We will assume for simplicity that each ball meets the wall with the same speed. Third, it depends upon how often the balls hit the wall; or put slightly differently, it depends upon how many balls hit the wall per second.

If then

m = mass of one ball,

v = velocity, or speed, of a ball,

n = number of balls hitting the wall in a second,

the pressure on the wall might be expected to be proportional to the product, mnv . Now a minute's reflection should serve to convince the reader that the number of balls hitting the wall per second is proportional to their speed; clearly if the balls move twice as fast and there is a steady stream of them, there will be twice as many impacts (if the purist is looking the other way we may yield to the temptation to say "biffs") per second. Hence n is proportional to v , and for mnv we can write mv^2 . Now try and see this as an illustration of what happens at the mouth of the gas jar. Consider a unit area—a square centimetre—(pressure in accurate work always means "per unit area" unless clearly otherwise stated) of the surface separating the gases before diffusion starts. m is now the mass of a molecule and v its speed. The pressure on both sides is the same, namely the atmospheric pressure. If then m and v be the values for the hydrogen and m' and v' for the air, we have, by expressing in algebra the fact that the two pressures are equal:

$$mv^2 = m'v'^2,$$

$$\frac{v}{v'} = \frac{\sqrt{m'}}{\sqrt{m}}.$$

By Avogadro's Law m and m' are clearly proportional to d and d' , the densities, and we get finally:

$$\frac{v}{v'} = \frac{\sqrt{d'}}{\sqrt{d}}.$$

This looks like a statement in symbols of Graham's Law. But it must be noted that the velocity is here the velocity of the individual molecules which is much greater than that of the actual diffusion of the gas. However, since the diffusion is caused by the velocity of the particles it may be taken that the one velocity is proportional to the other and on this assumption the equation is a statement of Graham's Law.

This is not a rigid proof; it is merely given to help the reader to see what happens. A rigid proof would, among other things, take into consideration the facts that the velocities are not all in one direction and are not all equal. But, at any rate, it makes the law seem a reasonable and likely one.

272. The explanation of the paradox that the lighter a gas the more readily it diffuses, even against gravity, may be summed up thus. We are comparing the gases at the same pressure and temperature. Under these circumstances equal volumes of different gases contain the same number of molecules. The pressure is caused by the movement of these molecules. Hence a light gas must compensate for its lightness—which would tend to decrease its power of producing a pressure—by the faster movement of its particles. If two spaces of equal volume were filled with the same number of molecules, one of a light gas and one of a heavy gas, moving on an average with the same speed, they would *not* be at the same temperature and pressure. The lighter gas would be at a lower temperature and would exert a smaller pressure. So, if the temperature and pressure are to be equal, the lighter the gas, the greater the velocity.

Chapter XXI

COMPOUNDS OF NITROGEN

1. AMMONIA

273. Some elements, such as sodium, are difficult to extract from their compounds, and when extracted it is difficult to keep them isolated. Sodium, for example, has to be kept under naphtha; it so readily oxidises. Other elements, such as aluminium, are difficult to isolate, but once isolated are kept in a free state without much difficulty. Nitrogen behaves in exactly the opposite way. It occurs in nature in vast quantities in the free state; it is easily separated from most of its compounds, and once it is free it is somewhat difficult to persuade it to combine with anything. Nitrogen compounds are important and valuable; they include the large class of indispensable food-stuffs known as proteins, various fertilisers for the soil, and the whole group of aniline dyes. The producing of compounds from the free nitrogen of the atmosphere is therefore a very important technical problem and one to which great attention has been given.

274. We have four main sources of nitrogen compounds.

(1) Mineral nitrates. Of these by far the most important is sodium nitrate or Chili saltpetre. This is found in the dry districts of the north of Chili, and its export is one of the staple industries of that country. This mineral has recently been found near Alice Springs in Central Australia, a discovery which may have very important developments.

(2) Animal matter. This includes stable refuse, horns and hoofs and any scraps of skins, leather and so forth which are otherwise useless.

(3) The nitrogen in the air. The production of compounds from this free nitrogen is called "fixing". There should be no need at

this stage to remind the reader that the air is a mixture, not a compound.

(4) The ammoniacal liquors and ammonium sulphate, produced in the gas works.

275. The more important of the simpler compounds of nitrogen are ammonia, NH_3 , and the compounds it produces when it combines with acids (the ammonium salts; see § 278); the oxides of nitrogen and the two commonest acids of nitrogen, nitric acid (HNO_3) and nitrous acid (HNO_2) with their salts the *nitrates* and the *nitrites*.

276. Ammonia, NH_3 , is the commonest and most important compound of nitrogen and hydrogen, the others being hydrazine, N_2H_4 , and azoamide, N_3H . The familiar household ammonia, so useful for cleaning spots off clothes because it dissolves grease, is really a solution of ammonia in water, pure ammonia being a gas.

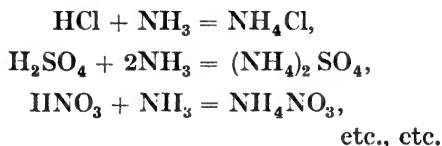
277. Nitrogen is an essential constituent of nearly all animal matter, and many animal substances when heated or when they decay or ferment give off this nitrogen combined as ammonia. Thus leather, skin, hair and many other such materials can serve as sources of ammonia by merely heating. The distillation of coal also yields a certain amount of ammonia—about $\frac{1}{2}$ per cent. by weight—and much of the ammonia of commerce is obtained in this way as a by-product of the gas works. This is one of the two most important sources of ammonia. The other is the direct union of nitrogen and hydrogen, which is now worked in this country as a commercial proposition, by the Haber process. This was originally a German method but is now being worked in England. There are three essential conditions for the direct union of hydrogen and nitrogen to take place—a very high pressure, a temperature of about 500°C . and a suitable catalytic agent. The actual pressure used is over a ton and a quarter to the square inch. Several catalysts have been found to be effective, the one in practical use being a fine powder of molybdenum and iron. A mixture of three volumes of hydrogen with one of nitrogen is

treated in this way, and from a quarter to a third of the whole is converted into ammonia.

Ammonia is also obtained synthetically by another but indirect process, the cyanamide process. It has been found that calcium carbide, CaC_2 , when strongly heated in nitrogen absorbs the gas to form calcium cyanamide, CaCN_2 . This can be used directly as a manure, or ammonia can be obtained from it by decomposing it with hot water or steam:

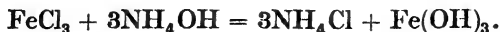
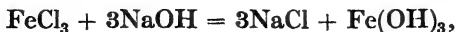


278. Ammonia readily combines with acids without any displacement of hydrogen. The reactions represented by the following equations take place easily and directly:



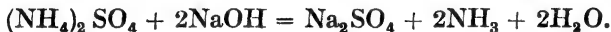
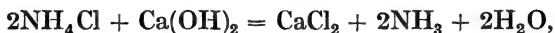
The compounds of ammonia produced in this way much resemble the salts of sodium and potassium. If the formulæ of these ammonia compounds be compared with those of the corresponding sodium salts—e.g. NH_4Cl with NaCl , and so on—it is seen that in each case the ammonia compound can be considered as the corresponding sodium compound with the sodium replaced by the group NH_4 . This group is referred to as **ammonium** and the salts as “ammonium salts”. These salts are usually white or colourless and are soluble in water, in both respects resembling the salts of sodium and potassium (see § 579). Why this should be is one of the many wonders of chemistry. Ammonium has no separate existence. Yet from a consideration of its salts it might almost be another metal. The solution of ammonia in water is alkaline and contains a compound, NH_4OH , similar in composition to NaOH and KOH , with which substances it has several properties in common. Compare, for

instance, their actions in solution upon a solution of ferric chloride:



In both cases the ferric hydroxide comes down as a rusty brown precipitate.

279. The salts of ammonium give off ammonia when heated with caustic soda, caustic potash or lime:

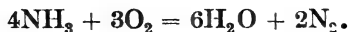


This is the commonest way of preparing ammonia in the laboratory. Ammonium chloride and plenty of slaked lime are mixed in a flask with a little water and gently heated, and ammonia is very readily emitted (see § 660). The water is added to diminish the risk of cracking the flask. As it is about the most soluble gas known it cannot be collected over water. It is very light and can be collected in an inverted jar preferably in a draught cupboard, the gas being very pungent and apt to be unpleasant in the open room. Or it can be collected over mercury.

280. If this is the usual way of producing ammonia, why is it introduced thus almost casually? Why is it not given as important a place as the manufacture from coal or by the Haber process, especially as it is the easiest process of the three? The reason may be better understood by recalling the old problem of which came first, the hen or the egg. Ammonium salts are practically always made from ammonia, and if ammonia is to be made from ammonium salts it is clear that we have here no real source of ammonia at all. The student will continually be reminded that nitrogen compounds are of first rate importance to man (see chap. xxiii for instance). Nor does it much matter whether the nitrogen be in the acid radicle of the salt, as in a

nitrate or nitrite, or in the position usually occupied by the metal as is the case with ammonium salts. Both ammonium sulphate and sodium nitrate are nitrogen compounds of the utmost practical importance. What is required is a source of nitrogen compounds independent of ammonium salts, which are rare in nature, and of nitrates, which are not much commoner. The reader will now see why the preparation of ammonia from an ammonium salt is only of secondary importance. Historically, however, this was the first way in which ammonia was prepared. This was by Priestley in 1774, who obtained it by heating sal ammoniac, NH_4Cl , with quicklime, CaO . Ammonium chloride occurs rarely as a mineral deposit and is also obtainable from certain organic matter. Since ammonia is so easily recovered from ammonium chloride, the salt provides a very convenient way of storing the gas. Ammonia is very light, not readily liquefied and very pungent. Ammonium chloride is easily prepared and stored and easily carried about. Hence it acts as a simple and useful source of ammonia, whenever the gas is required. Ten grammes of ammonium chloride will yield, when treated with quicklime, over 4 litres of gaseous ammonia, as the reader should be able to verify for himself.

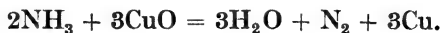
281. The formula NH_3 suggests that, as it contains so much hydrogen, ammonia would be inflammable. As a matter of fact under ordinary conditions it may be described as just not inflammable. Ordinary air is not sufficiently rich in oxygen. If ordinary air be replaced by a mixture of 4 parts of nitrogen with 13 of oxygen, ammonia will just burn in the mixture. In pure oxygen it burns readily enough, with a tawny flame:



This is not a "clean" reaction, traces of ammonium nitrate being formed as well. The reader will gather that the phrase "a clean reaction" is used to describe one which goes just according to the equation, without any secondary reactions.

A spiral of platinum wire heated to redness and suspended over the surface of strong ammonia solution remains hot, the temperature being maintained by the gentle combustion of the ammonia given off. The gas, however, does not catch fire. The wire may be conveniently suspended from a piece of cardboard in the neck of a flask, as in fig. 32.

282. The composition of ammonia may be determined either by weight or by volume. The method by weight consists in passing dry ammonia over red hot copper oxide, when the action is:



If, then, the steam produced be condensed and weighed and the volume of nitrogen liberated measured, we have sufficient data to calculate the composition by weight. The practical details are, however, troublesome, and the reader is advised to confine himself for the present to the methods of determining the composition by volume, when the details of the experimental work are much simpler, and good results can be obtained by the beginner.

283. The composition of ammonia by volume may be found directly, since an electric spark will decompose ammonia. A eudiometer tube, as already described, is used for the experiment. The tube is filled with ammonia and on sparking for a quarter of an hour or so the volume at first increases and then remains stationary. At this point most of the ammonia will be decomposed, though the sparking never decomposed it all. The unaltered ammonia can be removed by opening the tube over dilute sulphuric acid, and, taking the volume thus removed from the original volume, the volume of ammonia decomposed is found. This volume is seen to have been doubled by the decomposition. This is consistent with the equation

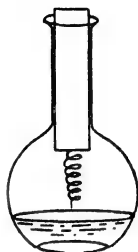


Fig. 32. Oxidation of Ammonia.

It will be noticed that three-quarters of the gas produced should be hydrogen. This can be verified by introducing enough oxygen to combine with this hydrogen on sparking. If any volume of oxygen up to three-eighths of the total volume of gas be introduced, there is a contraction on sparking. Any more oxygen introduced remains unchanged, and if it be absorbed by a piece of phosphorus the nitrogen remains, equal in volume to half the original ammonia used and so being one-quarter of the volume produced by the decomposition.

284. A slightly less direct method is the following. A graduated tube with a tap at each end is filled with chlorine (see fig. 33).

A funnel at the top contains a strong solution of ammonia. The top tap is opened and the ammonia admitted a drop at a time. There is a vigorous reaction accompanied by flashes of light as each drop falls in. The experiment must not be hurried or the apparatus will get too hot. The action is accompanied by the production of white fumes of ammonium chloride. The chlorine combines with the hydrogen of the ammonia, liberating nitrogen and forming hydrochloric acid which in turn combines with some of the unused ammonia; hence the fumes. When a few cubic centimetres of strong ammonia have been intro-

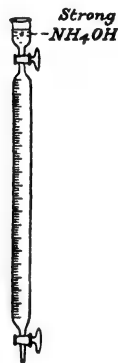


Fig. 33. Composition of Ammonia.

duced, all the chlorine has been used up. At this stage the top tap is turned off and the lower tap opened under water. Water enters, and when the level is adjusted so that the pressures inside and out are the same, the gas remaining—nitrogen—is seen to occupy one-third of the volume of chlorine at the start. But hydrogen and chlorine combine in equal volumes. So the volume of hydrogen in the ammonia equals the volume of chlorine used, which is three times the volume of nitrogen remaining. Ammonia, then, contains by volume three times as

much hydrogen as nitrogen. It will be noticed that the volume of the ammonia nowhere enters into the experiment, and so the experiment proves the percentage composition of ammonia but does not definitely establish the formula. If this be compared with the eudiometer method it will be seen that in that case the volume of the original ammonia and of each of the constituent gases was observed, and so that method justified the formula NH_3 . The chlorine method, however, establishes the formula NH_3 when considered with the fact that ammonia is 8.5 times as dense as hydrogen.

285. As a matter of fact, the formula NH_3 can be completely justified by considering the two following facts:

(1) The gas is composed of nitrogen and hydrogen and nothing else.

(2) The density of the gas is 8.5 ($H = 1$) and so its molecular weight must be 17.

For, since the atomic weight of nitrogen is 14 there can only be one atom of nitrogen in the molecule, as otherwise the molecular weight would have to be more than 28. This atom of nitrogen contributes 14 to the molecular weight. The other three, therefore, must be due to three atoms of hydrogen; hence the formula is NH_3 (compare this with H_2S , § 372).

286. It may be noted here that care must be taken in choosing a drying agent for ammonia. It combines, of course, with sulphuric acid to form ammonium sulphate. It also, rather unexpectedly, combines with calcium chloride. *This fact should not be overlooked.* It is common to use phosphorus pentoxide, P_2O_5 , as a drying agent. This is very effective. But it must be noticed that P_2O_5 is the anhydride of phosphoric acid. Hence if any water be present some acid will be produced and so some ammonia absorbed to form ammonium phosphate. If the pentoxide be used to dry ammonia, it is clear that in the very process of drying the ammonia it becomes capable of retaining

some of it. This must not be lost sight of in a quantitative experiment. Ammonia can be conveniently dried by quicklime, CaO , or *solid* caustic soda, NaOH . Phosphorus pentoxide is used to remove the last traces of moisture.

287. We have seen that ammonia is a light gas very soluble in water, the solution having an alkaline reaction. The pungent and not unpleasant smell is characteristic. Incidentally it is curious to note how very often a remarkable odour is possessed by a compound of a non-metal with hydrogen. In addition to ammonia there is SH_2 , with a smell of rotten eggs, and SeH_2 and TeH_2 with odours much like SH_2 . PH_3 smells like decayed fish, and AsH_3 and SbH_3 have each a powerful smell of onions. Some, but not all, of the many compounds of hydrogen with carbon have penetrating and curious odours. The smell of the hydride of boron, BH_3 , is described by those who have experienced it as extremely disagreeable. The hydride of silicon, being spontaneously inflammable in air, is deprived of any opportunity of exhibiting its powers of affecting the nose. This series of odours is quite notable and may one day be used to throw some light on the nature of smells. The coincidence is far too striking to be a pure accident.

288. The presence of ammonia is usually observed by the smell. In very small quantities it can be detected by **Nessler's solution** (see § 660). If a solution of potassium iodide be added to a solution of mercuric chloride, a precipitate is formed which is at first yellow and almost at once turns red. On adding more potassium iodide the red precipitate dissolves. At this stage potassium hydroxide is added and this forms Nessler's solution. A small trace of ammonia is sufficient to turn this solution brown.

Chapter XXII

COMPOUNDS OF NITROGEN

2. OXIDES AND ACIDS

289. Nitric acid, HNO_3 , is conveniently prepared from a nitrate. Large quantities of mineral nitrates are mined in northern Chile, and this supply is a very important natural source of nitrogen compounds. To obtain the acid from the salt the latter is heated in a retort with concentrated sulphuric acid. The retort is arranged as in the figure, the neck passing down into a flask

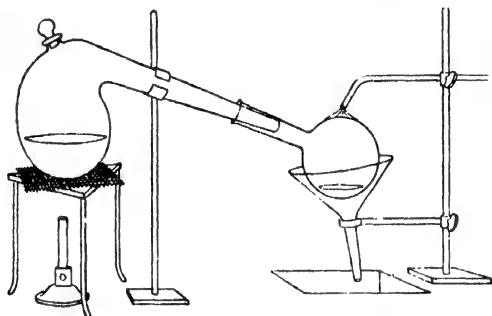
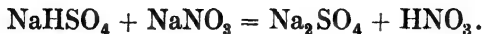


Fig. 34. Preparation of Nitric Acid. (See Plate V.)

surrounded by cold water. In this the acid condenses and is collected (see fig. 34). The equation is



or, with more nitrate and at a higher temperature than is practicable in an ordinary laboratory,

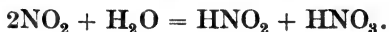


At this higher temperature the nitric acid is decomposed to a considerable extent. The former reaction is therefore used and

the acid is distilled off under reduced pressure. This enables a lower temperature to be employed and so prevents decomposition.

290. Nitric acid produced in this way is a very corrosive substance. It acts upon the skin, making painful sores which heal with difficulty. The first effect is to turn the skin yellow. This is a characteristic effect of nitric acid on proteins and certain other organic nitrogen compounds. It is called the "xanthoproteic" reaction. The acid gives off strong fumes and is very destructive, too, to clothing and so must be handled with great care.

291. Nitric acid can be made on a commercial scale by the oxidation of ammonia. The ammonia is mixed with oxygen and passed over heated platinum gauze which acts as a catalytic agent. By this means the bulk of the ammonia can be oxidised to water and nitric oxide, NO. The latter will combine directly with oxygen to give nitrogen peroxide, NO₂, which reacts with water thus:



In this way nitrous and nitric acids can be produced. In actual practice a much higher yield of nitric acid is obtained. This is done by passing the nitrogen peroxide, mixed with air, down tall towers packed with pieces of broken stone over which water is kept trickling. Thus the mixed nitrous and nitric acids are exposed to the air over a large surface and under these circumstances most of the nitrous acid is oxidised to nitric. This method of obtaining a large effective surface should be compared with the similar device used in the manufacture of sulphuric acid. By using an alkali (e.g. NaOH or Ca(OH)₂) with the water a nitrate can be produced instead of nitric acid.

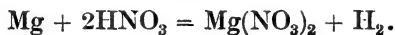
292. Nitric oxide is also made directly from nitrogen and oxygen. This requires an exceedingly high temperature which is secured by electrical means. The yield in this case is much smaller than in the manufacture from ammonia, and the consumption of power is greater but the ingredients are cheaper. Hence it is used in Norway, a country which has an abundance

of easily available and therefore cheap water power. The process, however, is passing out of use as being too expensive.

293. Pure nitric acid is colourless, but it readily decomposes, especially in daylight, giving oxides of nitrogen. These colour the acid which in an ordinary glass bottle may be any colour from light yellow to a dark mahogany brown.

294. Nitric acid is both a strong acid and a strong oxidising agent. The latter property must never be forgotten in considering what the effect of nitric acid is likely to be in any chemical action. The fact that it belongs to two important classes of reagents—acids and oxidising agents—makes its actions frequently rather complicated. Generally speaking, when dilute, the oxidising action is somewhat masked. The instruction “add nitric acid” or the statement “the action of nitric acid is so-and-so” is of little help unless more particulars as to the concentration of the acid are given.

295. Viewed purely as an acid it might be expected to act upon zinc and some other metals with liberation of hydrogen. This does happen with magnesium and dilute acid:



But it is quite the exception for such a simple action to occur. Nitric acid readily parts with oxygen, with which hydrogen readily combines, and the result is that the hydrogen is oxidised to water. What happens to the nitric acid may conveniently be seen by regarding the acid as the combination of water with the anhydride, N_2O_5 . The hydrogen removes oxygen from the latter and leaves a lower oxide of nitrogen or free nitrogen. It may even go beyond this stage. There being no more oxygen to remove, the hydrogen combines with the nitrogen to yield ammonia. This is an example of the general principle that the addition of hydrogen is regarded as reduction just as much as is the subtraction of oxygen. Of course, when ammonia is produced in this way it combines with some of the nitric acid to give ammonium nitrate.

Some ammonium nitrate is produced when Mg is dissolved in HNO_3 . The actual reactions which occur are, however, not quite so simple as this suggests. It will be as well to consider the oxides of nitrogen before pursuing this question further.

296. There are at least five oxides of nitrogen:

N_2O , nitrous oxide.

NO , nitric oxide.

N_2O_3 , nitrogen trioxide or nitrous anhydride.

NO_2 or N_2O_4 , nitrogen peroxide.

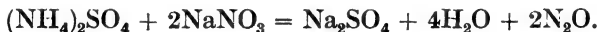
N_2O_5 , nitrogen pentoxide or nitric anhydride.

Nitrous oxide is usually prepared by heating ammonium nitrate crystals:



(see § 669). This will not be unexpected if the reader recollects how nitrogen was prepared from ammonium nitrite (see § 136). **The beginner is advised not to try this experiment** without proper guidance, as under some circumstances **ammonium nitrate is dangerously explosive**.

If no ammonium nitrate is available, sodium nitrate may be heated with an ammonium salt, e.g.



Nitrous oxide is also liberated when *dilute* nitric acid acts upon zinc. The gas is somewhat soluble in cold water and should be collected over hot water.

297. Nitrous oxide has three very striking properties:

(1) It supports combustion even more vigorously than pure oxygen. Considering that it contains only half its own volume of oxygen, this is surprising. But oxygen and nitrogen do not readily combine to form nitrous oxide. A certain amount of energy disappears in the process of making them combine. When they part company this energy is liberated again in the form of heat,

hence the briskness of the combustion when, say, a match burns in nitrous oxide. This will be clearer after reading chap. XXIII.

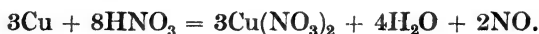
(2) Nitrous oxide is an anaesthetic. When inhaled it produces complete unconsciousness and insensibility to pain. It is used for small surgical operations, such as drawing teeth. It cannot be used safely to produce anaesthesia for any length of time.

(3) Nitrous oxide and air when inhaled together are liable to induce hysterical laughter. This is a very odd phenomenon and must be experienced to be fully appreciated. It brings home with great vividness the old Latin saying:

“Incepto risu ineptior res nulla est.”

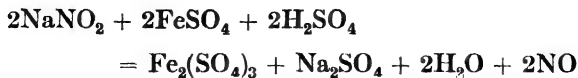
The gas has a slight sweetish taste and smell. Substances burnt in the gas are oxidised and a volume of nitrogen remains equal to the original volume of nitrous oxide. The reader should have no difficulty in seeing how to justify the formula N_2O . This will, of course, necessitate finding by experiment *either* the density *or* the percentage composition.

298. Nitric oxide, NO. This oxide is a colourless gas which is emitted freely when nitric acid acts upon copper (see § 667). The nitric acid must be diluted with its own volume of water. The main reaction is

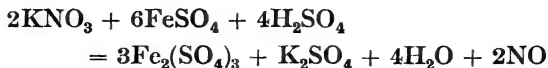


The gas being insoluble can be collected over water. When prepared by this method the nitric oxide obtained is not pure. If the gas be passed into a solution of ferrous sulphate, $FeSO_4$, it dissolves to form a brown solution. On heating this solution pure nitric oxide is given off.

The gas may also be prepared by warming a mixture of ferrous sulphate and sodium nitrite in solution with dilute sulphuric acid:



(see § 667), or by pouring cold concentrated sulphuric acid on to powdered potassium (or sodium) nitrate and then adding a saturated solution of ferrous sulphate:

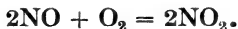


(see § 668). When prepared by either of these two methods the nitric oxide is obtained pure.

The direct production of nitric oxide from oxygen and nitrogen has already been referred to (see § 292).

299. When a piece of sodium or potassium is heated in a volume of nitric oxide, it combines with the oxygen and the residual nitrogen is found, at the same temperature and pressure, to occupy half the volume of the original nitric oxide. The density of the gas is, by experiment, 15 ($H = 1$). Hence the molecular weight is 30. As the gas contains nothing but nitrogen and oxygen, the atomic weight of oxygen being 16, there cannot be more than one atom of oxygen in the molecule. 30 minus 16 is 14, the atomic weight of nitrogen. Hence there is one atom of nitrogen in the molecule and the formula is NO. The reader will easily see how this agrees with the fact that, on removal of the oxygen by potassium, the resulting volume of nitrogen occupies half the volume of the original nitric oxide.

300. There are two specially remarkable things about nitric oxide. One is that it combines at once with oxygen to produce rusty red fumes of nitrogen peroxide:



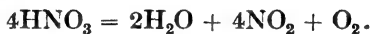
Thus the gas must not be allowed access to air. It is a very striking reaction. There is no other gas which does anything like it. It will be noticed that this can be used as a test for the gas or as a test for *free* oxygen. The other remarkable thing about nitric oxide is its formula. Nitrogen is usually regarded as tri- or quinquevalent. Oxygen is bivalent. The formula NO does not

fit in with both these facts. It is hopeless to try and explain this. The theory of valency so far as we have discussed it gives us no help here. The density of the gas is, as stated above, 15, and there is no evidence from vapour density or otherwise for the existence of any molecules of the formula N_2O_2 .

301. Nitrogen peroxide, NO_2 , is given off when many nitrates are heated, e.g.



The gas is commonly made by heating a nitrate in this way and the same reaction provides a means of making a basic oxide. Nitric acid itself on heating undergoes a similar decomposition, which, however, is only complete at a temperature well above its boiling-point:



The nitrates of the alkali metals act differently. They yield, on heating, oxygen and a nitrite:



302. Nitrogen peroxide is a rusty brown gas, which we have already seen combines with water giving both nitric and nitrous acids. It cannot therefore be collected over water. If it be passed through a U-tube standing in a freezing mixture of salt and ice, the gas is condensed to a brown liquid and this is the most convenient way of collecting it.

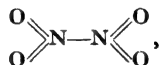
Nitrogen peroxide has a most penetrating and pungent smell and is very corrosive. It is injurious to health and should be treated with caution.

303. The density of nitrogen peroxide at ordinary temperatures corresponds neither to the formula NO_2 nor to N_2O_4 , but to something between. At a temperature of 150°C . the density corresponds to the formula NO_2 and the gas expands regularly in

accordance with Charles' Law up to about 200°C . Above that temperature the density decreases owing to the gas dissociating into nitric oxide and oxygen, the degree of dissociation increasing as the gas is still further heated. The red-brown colour of the gas is darkest between 150° and 200°C . This colour appears to be proper to the molecule NO_2 . Below 150°C . the gas seems to consist of molecules of NO_2 and of N_2O_4 mixed, the latter increasing as the temperature falls. When the gas is liquefied the colour remains, suggesting that even in the liquid form there are still some molecules of NO_2 . At very low temperatures the colour entirely disappears, and so, presumably, do the molecules of NO_2 . If the reader looks back to § 296 he will find it stated that there are "at least" five oxides of nitrogen. "At least" is the right phrase; for there is no reason why NO_2 and N_2O_4 should not be called different oxides. Molecules of NO_2 and N_2O_4 are commonly both referred to as "nitrogen peroxide", but this is just a matter of habit.

304. The remaining two oxides of nitrogen, nitrogen trioxide and nitrogen pentoxide, are as substances unimportant. They are, however, of great theoretical interest as the anhydrides of nitrous and nitric acid respectively.

305. The difficulty as to the valency of nitrogen in these compounds is a little eased when the oxide N_2O_4 is contemplated. This can be written



where the valencies are normal. One is somewhat happier in accepting the abnormality of NO_2 when one realises that it at any rate does sometimes fit into the scientist's scheme of things by forming double molecules. The action of nitric oxide judged by our carefully built-up theory appears quite irregular. There is no evidence whatever of any double molecules. The chemist must look the difficulty squarely in the face—and pass on.

The above expresses a little exasperated impatience with

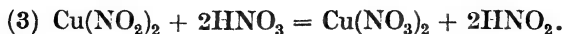
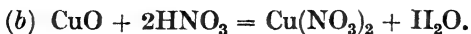
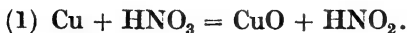
nitric oxide. Yet the scientist must not forget that there is nothing whatever wrong with this oxide nor with the formula for it. The difficulty rests entirely in his own limitations. Nature may appear perverse, but she is never wrong. The scientist often is.

306. Now that the reader is acquainted with the oxides of nitrogen he will be able to understand a little better the action of nitric acid upon metals.

For many years two rival theories have existed. According to one, the first product of the action of a metal, such as copper, on nitric acid is to produce hydrogen, which then reacts with more nitric acid and yields products which vary with the concentration of the acid, the temperature and the character of the particular metal used. In support of this it is urged that when nitric acid acts upon magnesium hydrogen is produced. According to the other view no hydrogen is produced and the metal itself acts as the reducing agent.

Some recent work (1930) indicates that there is truth in both these theories. When copper or silver acts on nitric acid, copper oxide or silver oxide is first formed and nitrous acid is produced. If the nitrous acid as it is formed is removed from contact with the metal, the metal only dissolves very slowly. This removal may be effected by the addition of urea ($\text{CO}(\text{NH}_2)_2$), hydrogen peroxide, or potassium permanganate to the solution. Or it may even be effected mechanically by rapidly rotating the metal.

It is suggested that the following are the reactions:



In dilute acid 4 (a) gives nitric oxide as the main product, but in concentrated acid 4 (b) preponderates and nitrogen peroxide is the most abundant product. In most cases a mixture of the two gases is found.

307. In contrast with copper, it appears that tin, iron, zinc and magnesium do not produce any nitrous acid. The first product with dilute acid is probably hydrogen, which then reacts with more acid to form various products which vary according to the concentration of the acid used and the character of the metal employed, e.g. nitrous oxide, nitrogen, ammonia (which will combine with nitric acid to form ammonium nitrate) and a compound called hydroxylamine, NH_2OH .

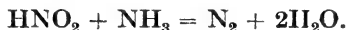
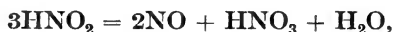
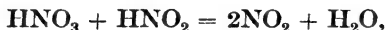
With concentrated acid acting on the metals tin, iron, zinc and magnesium, it would appear that the oxidation reaction preponderates. Tin and iron form two excellent examples. Tin dissolves in dilute nitric acid giving stannous *nitrate*; the hydrogen reduces the nitric acid mainly to ammonia; but with concentrated acid a hydrated stannic *oxide* is produced (it should be noticed that this compound has not the requisite physical properties to form a good protective coating). Similarly iron dissolves in dilute nitric acid, but in concentrated acid the acid receives a thin film of ferric oxide which protects it from all further action—even action from other acids—and the iron is said to be “passive”.

308. When considering these suggestions it is well to remember that tin, iron, zinc and magnesium liberate hydrogen from hydrochloric acid or sulphuric acid; there is therefore some reason for expecting them to liberate hydrogen from nitric acid. Copper and silver, on the other hand, do not liberate hydrogen from hydrochloric acid or sulphuric acid, and there is no reason to expect them to liberate it from nitric acid.

309. It has been contended by some investigators that the oxides of nitrogen are *not* the *direct* products of the reduction of nitric acid; these are held to be nitrous acid (HNO_2), hypo-

nitrous acid ($\text{H}_2\text{N}_2\text{O}_2$), hydroxylamine (NH_2OH) and ammonia (NH_3).

310. It will be seen that these compounds can be regarded as formed from nitric acid by the removal of oxygen or addition of hydrogen. The formation of nitrogen peroxide, nitric oxide, nitrous oxide and nitrogen is regarded as due to reactions between the above-mentioned compounds or between some of these compounds of nitric acid, e.g.



All these reactions are possible and most of them are known to occur if the compounds shown are brought together; but this is not by itself convincing evidence that these are the reactions which occur when a metal acts upon nitric acid.

Chapter XXIII

CHEMISTRY, ENERGY AND LIFE

311. If the question is raised as to what is the most real and practical object of chemistry, the obvious answer is that the object is the preparation of useful substances. But there is another aspect of the matter. A very useful function of chemistry lies in the control it gives over *energy* changes, and many of the chemical actions that man sets going have the liberation of energy as their end in view. Sometimes it is a sudden liberation of energy, as occurs when a charge of dynamite is exploded to break a rock; or it may be a steady and constant supply of energy as is the case of the burning of fuel in a steam engine or the operation of an electric battery.

312. The more detailed study of energy is considered in the science of mechanics. We may remind the student here that energy is the capacity for doing work and that the most usual forms of energy are heat, electrical energy, light and other forms of radiant energy including the ether vibrations used in wireless, sound, kinetic energy (the energy a body possesses because it is moving) and potential energy (the energy a body possesses because of its position). It is possible to measure all these different kinds of energy in the same units such as ergs or calories and to compare them quantitatively.

313. It has been shown that there is a law of **Conservation of Energy** similar to the law of the Conservation of Mass. Whatever changes take place there is never any creation or destruction of energy. There are only changes from one kind to another.

Consider, for example, the following case. A large stone is at the top of a cliff. It has some potential energy by reason of its position. If it is pushed over the cliff, gravity will do some work

during its fall. While it is falling its *potential* energy decreases and an equal amount of *kinetic* energy appears instead. Suppose the stone reaches the end of its fall and is stopped by the ground. All the kinetic energy disappears. Some sound is produced, which, however, only represents a very little of the energy. The bulk reappears as heat; the stone and the ground where it fell both rise in temperature and the calories of heat produced (plus the small amount of energy dissipated as sound) are equal to the kinetic energy immediately before impact, which is again equal to the difference in potential energy of the stone in the two positions, at the bottom and at the top of the cliff.

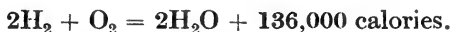
314. Now compare this case with the following. A piece of phosphorus is outside a jar of oxygen and both are at the temperature of the room. The phosphorus is placed in the jar and at once a vigorous chemical action takes place, a new white substance, an oxide of phosphorus, P_2O_5 , is produced and much energy—heat and light—is evolved. Where has this energy come from? If we return to the case of the stone falling off the cliff, we see that a rearrangement of the relative position of the stone and the earth is attended with the liberation of heat energy and loss of potential energy. Similarly, the system consisting of phosphorus and oxygen contains energy within itself, i.e. *internal chemical energy*, which is much like potential energy. The same matter may exist in different chemical combinations, and each combination contains a different amount of internal energy. If we pass from a form of large internal energy to one of less, the difference will appear in the chemical action mainly as heat. If we want to reverse the process, we must put into the action just as much heat as was evolved. Thus a gramme of carbon gives out about 8000 calories when it is burnt in oxygen to form CO_2 . Hence to split CO_2 into C and O_2 would involve the disappearance of 8000 calories per gramme of carbon liberated, or, if it could be done by an electrical method, an amount of electrical energy exactly equivalent to 8000 calories would be absorbed. In practice,

it is usually necessary to supply a lot more heat than is actually absorbed, but only the amount required disappears in completing the reaction.

315. Since energy is quite as important as matter, it is clear that the ordinary chemical equation is not as complete as it might be, since it says nothing about the energy changes. This can be remedied by putting the amount of energy liberated by a reaction into the equation. If every molecule on the left-hand side is treated as a gramme-molecule and the energy liberated is measured in calories, the latter can be shown on the right-hand side. Thus the burning of a gramme-atom of carbon is expressed thus:



and of two gramme-molecules of hydrogen:



316. An action of this sort which is attended with a liberation of energy is said to be **exothermic**. If the action absorbs heat—i.e. heat must be supplied to cause it, this heat disappearing in the process—the action is **endothermic** and the heat absorbed is placed on the other side of the equation.

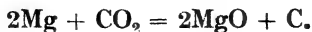
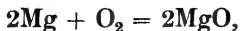
317. Thus, for example, if by any means carbon dioxide is split up into carbon and oxygen, the equation would be



or, if preferred,



Magnesium, for example, burns in oxygen or in carbon dioxide. If 48 gm. of magnesium is burnt in oxygen and another 48 gm. in carbon dioxide, 97,000 calories of heat less would be liberated in the second case than in the first. (Atomic weight of magnesium is 24.) This will be clearer on examining the equations



It will be noticed that in the first case the magnesium combined directly with the oxygen. In the second the heat necessary to decompose the CO_2 had to be supplied and so this heat disappears in the course of the action.

318. The student must keep his mind clear on one point here. The heat required to *start* the action is not the heat referred to above. It is not an *amount of heat* but a *temperature*, not *calories* but *degrees*, that induces an action such as the burning of carbon or hydrogen to start; it then goes on spontaneously with evolution of heat.

319. The two big principles of *conservation of energy* and *conservation of mass* occupy a fundamental position in science. Their importance can scarcely be overrated. They are the two legs on which the whole body of science stands. Once the reader has grasped and accepted them he cannot but feel he has made a real advance in understanding the world in which he lives and moves and has his being.

320. An ingenious gentleman once decided he could make his fortune by running a cat and rat farm. The cats were to feed entirely on dead rats and the rats entirely on dead cats. The skins of both were to be sold to yield the profits, and the farm was to go on for ever. In criticising this scheme the most obvious flaw is that it violates the principle of conservation of mass. A certain weight of material in cats and rats is there to start with, say 5 tons. If skins are being sold and there is no outside source of food, the total matter in cats and rats is continually decreasing and things must come to a stop. Or, put differently, the total weight of furs sold could never exceed 5 tons, the total weight of cats and rats with which the farm was started, and would in fact be much less. It is equally true, though perhaps a little less obvious, that the scheme violates the law of conservation of energy. There is a certain amount of energy in the chemical material of cats and rats at the start. Much of it is being used up by the beasts—they dissipate energy in sounds, their bodies are hot and as they tend

to cool this heat must continually be renewed, and they use a certain amount of energy as they scamper about. This means a steady and rapid loss of energy which, were no food other than the rats and cats used, would be seen in a steady decrease in the number of animals. Now enlarge the idea. Consider all the animals on the earth. If they were all carnivorous and lived on each other, the whole stock would go the way of the cat and rat farm. The proposal to sell the skins is just a commercial accident. The energy question is more important than the mass question. Now what happens to the carbon in some complex compound in an animal's body? The complex compound breaks down into simpler compounds and in the process yields energy for the creature's activities. The most likely fate for the carbon is to be turned ultimately into carbon dioxide and breathed out by the animal's lungs into the air. If, then, there were no reverse process the carbon dioxide in the air would increase, there would be less and less carbon with chemical potential energy (and this practically means carbon not combined with oxygen) and animal life would stop. But it does not stop, because some animals are herbivorous. They get their carbon in a form possessing plenty of energy from the plants they eat.

321. So far so good. But there is obviously something incomplete in our description. Why does not the air become full of carbon dioxide instead of oxygen? Why do the plants not get used up? The answer here is, that the plants are the centres of the reverse process. They have the power of feeding on the carbon dioxide in the air and building it up into substances with much chemical energy—starch, sugar, cellulose and the like. It is a very striking fact that many of these vegetable food-stuffs contain carbon, hydrogen and oxygen, the two latter in exactly the same proportions as they exist in water. That means that, if a plant builds up such a compound from carbon dioxide and water, all the oxygen in the former is restored to the air. For every 12 gm. of carbon an animal breathes out, it has used up 32 gm. of

oxygen; for every 12 gm. of carbon in the form of carbon dioxide which a plant uses, it restores 32 gm. of oxygen to the air. The balance is perfect. But this is only from the point of view of conservation of matter. What of the conservation of energy? If the plant takes up the inert carbon dioxide and makes it into starch, sugar and the like, it must have some energy put into it. What is the source of this energy? It has come from the radiant energy of the sun. "Radiant energy" here is a wider word than light. Light is that part of the sun's radiant energy or radiation which affects the eye, and that is by no means the whole. The arrangements by which the plants make use of this radiation are most interesting. On the surfaces of leaves—more particularly the under-surfaces—are minute openings called "stomata", into which the air, with its carbon dioxide, passes. Here it meets with a wonderful green substance, **Chlorophyll**. If one substance more than any other in the whole of nature is calculated to excite our wonder, our admiration and our gratitude, it is chlorophyll. That to it is due the tender green of spring and the restful colour of grassland and woodland is the smallest of its blessings. For without it no food could exist. The whole world of life, animal as well as vegetable, lives on the energy of the sun, and it is by the agency of this beneficent substance chlorophyll that we are able to get it. The Shintos of Japan worship the sun. An intelligent Shinto must surely make of chlorophyll an archangel. It would seem obvious to the uninitiated that a plant gets its substance from the earth. But we now see that this is not so. The main bulk of the solid material of a plant comes from the air and from water—which means, of course, rain, dew and the water vapour in the air.

322. If the reader has followed the description thus far, he will be able to give an answer to the question: What is the difference between a plant and an animal? To be sure, one is not likely to confuse a lion with a dandelion nor a tiger with a tiger-lily. The names of the snapdragon and the periwinkle do not deceive. But

there are cases among lower creatures when the point is really in doubt. A sponge, for example, is an animal and a bacillus is a plant. Where are we to draw the line? Well, in cases where we can determine whether an organism feeds on carbon dioxide by the aid of sunlight and liberates oxygen, or whether it only takes in oxygen and gives out carbon dioxide, we have a real test and a real distinction. There lies, broadly, the gulf fixed between the animal and vegetable kingdoms. There are, however, certain plants like the dodder or the mushroom which evade their duties. For an account of this the reader must refer to treatises on botany. It should be noted here that plants *do* use up oxygen and give out CO_2 , as animals do. In sunlight the production of oxygen is so great as to mask this. In the dark, however, the production of oxygen ceases and the production of CO_2 alone takes place. Thus at night plants not only restore no oxygen to the air, but tend to use it up. This is why they are best removed at night from a sick room.

323. But our full debt to the sunlight and chlorophyll partnership is not yet told. It supplies us, too, with wood and so indirectly with coal, so that, in addition to our food energy, the energy of our fuel comes from the same source. Truly has coal been styled "bottled-up sunlight". It is quite certain that coal is the remains of the vegetation of years long past. The exact origin of mineral oils—petrol and the like—is not so certain, but the modern view is that they, too, are of organic origin.

324. The reader will do well to compare the energy changes in carbon we have been discussing with the following. The sun evaporates water from the valleys which is deposited as rain on the hills and thus in stream and waterfall it gives us water power—a source of energy originally due to sunlight. The water on the mountains has acquired gravitational potential energy from the sun. Here we have a source of solar energy in useful form, not due to chlorophyll. It is worth while thinking this over. The giving of chemical potential energy to carbon in a plant is in

some ways like the giving of energy of position—i.e. gravitational potential energy—to rain deposited on high ground.

325. Another point in this remarkable story may be noted. The solubility of carbon dioxide in the sea is sufficient to be a matter of considerable importance. If the amount of this gas in the air were considerably increased, about five-sixths of the increase would be dissolved up in the sea. On the other hand, if the amount in the air were to decrease, the sea would yield up some of what is already there in solution. The effect of the sea is thus to diminish any change in the amount of carbon dioxide in the air. It acts as a moderating influence to keep the pressure of carbon dioxide in the air fairly constant. It will be noted that the carbon dioxide produced by burning, by slow combustion or by the decaying of vegetable or animal matter is used up by plants and its oxygen restored with the rest.

326. The liberation of oxygen by plants can be shown by placing a sprig of mint in a jar of water, standing inverted in water, and putting it out in the sun. Bubbles of oxygen are liberated and, when collected, will rekindle a glowing splinter.

327. The case of nitrogen in food-stuffs is as interesting, as important and as curious as that of carbon. The important class of food-stuffs called *proteins* is absolutely essential to life, and proteins all contain *nitrogen*. They include albumen (egg-white) and globulin (important in meat), casein (in cheese), legumen (in peas and beans), gluten (in wheat), etc. Nitrogen exists free in the air, and it was for a long time a complete mystery to scientists how this inert gas was built up into compounds of large chemical energy, and where that energy came from. It is now known that there are lowly organisms which live in the roots of certain plants which are responsible for the miracle. Of these organisms there are two kinds. The first kind build free nitrogen into *nitrites*, and the second feed on the *nitrites* and produce *nitrates*. The plants which harbour these effective but obscure workers in their roots all belong to one order, the leguminous

plants, a very large and varied group including peas and beans, vetches and clovers, gorse, broom, wistaria, laburnum and many others. These will be recognised as having butterfly-shaped flowers. It is easy to see why they include many important food crops, both for man and cattle, more particularly cattle. Vegetable protein is farther removed in structure and composition from the protein found in man than is the protein in beef or mutton. It is therefore simpler to let the cow or the sheep deal with it first, and to bring it a step nearer to the form in which man ultimately wants it, and then to use it as human food. Vegetarians might care to consider this point.

328. A recent report (1930) throws an interesting new light on the fixation by plants of nitrogen from the air. It states that "fixation is a function resorted to only in the absence of sufficient available fixed nitrogen". For non-leguminous plants fixed nitrogen in the soil is of great importance and all agricultural experience tends to prove that it is impossible to grow wheat, for instance, in soil without sufficient nitrogen in a form in which the plant can assimilate it.

So far we have only traced the fixation of nitrogen to the nitrate stage. In the past it has been taken for granted that the plant itself finished the process of turning this into protein. But more recent evidence shows that bacteria in the soil play an important part in this stage, too. Proteins cannot be built up from nitrates or from ammonia only. Carbohydrates are also necessary, and these can be produced from straw and stable refuse, again by the action of bacteria.

329. Since the organisms in the plant roots obtain their energy from the plant and the plant, with the help of chlorophyll, from the sun, it will be seen that indirectly this energy comes from the same source as the energy of the carbon compounds which do not contain any nitrogen.

330. The nitrifying organisms normally exist in the soil. The student will be able to see for himself why a crop of clover or

vetch can with advantage be grown on a piece of land before growing, say, wheat, why the advantage is greater if the clover be ploughed in without being gathered, why nitrates are used in artificial manures, and why peas will not grow in soil if it has been just previously baked.

331. Now that the need of nitrogen in the soil is well understood, the farmer need not rely on organisms in the soil nor upon leguminous plants. He treats the soil directly with manures containing combined nitrogen. The problem of "fixing" atmospheric nitrogen artificially is thus of enormous importance in the production of manures. In the past stable and farmyard refuse, which contain nitrogen compounds, and mineral nitrates were used for this purpose, and they still are, but modern chemical manures have now an enormous range of application. The reader may refer back here to the chapters on nitrogen compounds and he will meet with other chemical manures when he studies phosphorus and potassium (see §§ 391, 506, 507 and 508). The production of artificial manures is one of the many tremendous contributions to human welfare made by the science of chemistry.

Chapter XXIV

SULPHUR AND ITS COMPOUNDS

332. Sulphur has been familiar to man from the earliest times as a lemon-yellow solid. It is specially abundant in volcanic districts and hence is commonly associated with the infernal regions, a relic of the days when Pluto and his court were regarded as being in charge of such matters.

333. Sulphur occurs plentifully in nature in an uncombined state. It also occurs in many mineral sulphides—iron pyrites, FeS_2 ; galena or lead sulphide, PbS ; copper pyrites containing sulphides of iron and copper, $\text{CuS} \cdot \text{FeS}$, and a number of others. Of these, iron pyrites is a commonly used source of sulphur compounds; the others are usually of more interest for the metal they contain than for the sulphur. Several sulphates occur as familiar minerals—calcium sulphate or gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; barium sulphate or heavy spar, BaSO_4 ; also SrSO_4 and PbSO_4 . Soluble sulphates occur, too, in sea water and many mineral waters. Sulphides are usually insoluble in water while most sulphates are soluble. Hence among solid minerals there are found a greater variety of sulphides than of sulphates. Kieserite, however, occurs as a solid mineral though it consists of the soluble sulphate, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. It should be obvious why insoluble solid minerals are so much commoner than soluble ones (see also § 507).

334. Sulphur is an essential constituent of organic matter. In particular, proteins (see chap. XXIII) always contain sulphur, though not in large quantities. A silver egg-spoon becomes tarnished with a film of sulphur sulphide, Ag_2S , from the sulphur in the albumen, and it is this sulphur which is largely responsible for the odour for which bad eggs are justly famous. Coal contains

a little sulphur and it is no doubt from this source that traces of sulphur compounds get into the air in a room and necessitate the eternal polishing of silverware which is such a persistent nuisance to the housewife.

335. Up to the end of the last century the main sources of the supply of sulphur were the volcanic districts of Sicily and the mainland of Italy. The sulphur here occurs "native", i.e. as an element and not in combination. The question of preparing it is thus just a question of separating it from earth and other impurities. Sulphur is easy to melt and not difficult to boil, and so the purification is fairly simple. The sulphur is melted and the liquid run off from the solid material, after which it is further purified by being vaporised and the vapour condensed. The heat required for these processes is obtained by burning some of the crude sulphur, which is obviously an economical arrangement as the sulphur is very plentiful and consequently cheap. More recently, large deposits of sulphur have been found in the southern states of the U.S.A. This sulphur is obtained from deep shafts in the earth by a very ingenious process, depending for its efficiency on the melting of the sulphur by superheated water, i.e. water heated under pressure to some 70° above its normal boiling-point. Obtained in this way the sulphur is very pure and for most purposes requires no further special cleaning.

Sulphur obtained by cooling the vapour is a yellow powder called "Flowers of Sulphur". Sulphur is frequently melted and run into moulds giving solid sticks known as "Roll sulphur".

336. The element exists in a number of allotropic modifications. The familiar yellow sulphur is "rhombic" sulphur, a term which the reader should note but which he will not understand until he comes to a more detailed study of crystal shapes. He is advised not to worry about the term further at this stage unless he happens to have a special flair for solid geometry.

337. Rhombic sulphur has a specific gravity just over 2. It is insoluble in water but dissolves readily in a number of other

liquids, notably carbon disulphide, CS_2 . This substance is very volatile, and excellent rhombic crystals of sulphur can be obtained by allowing the CS_2 to evaporate on a watch-glass from a solution in this liquid. The melting-point of rhombic sulphur is 114.5°C ., at which temperature it turns to a mobile liquid. On further heating the liquid begins to get thinner, as is normally the case when a liquid is heated, but at 156°C . it thickens and the thickening process goes on until at temperatures over 200°C . the molten sulphur is very viscous and nearly black; it hardly "runs" at all. From about 250°C . onwards it gets thinner again, though it is never as thin as it was when first melted. At 444.5°C . it boils and turns to an orange-coloured gas. The vapour density at first is abnormal, but at very high temperatures—over 1000°C .—it is normal for the molecular formula S_2 . That is to say, the vapour is then 32 times as heavy as hydrogen, the atomic weight of sulphur being 32. Between the boiling-point and 1000°C . the density is too big for this formula and appears to consist of mixed molecules of S_2 and S_6 , with probably some of S_4 or even of S_8 . It is not uncommon to find that the molecules of a gas get simpler at higher temperatures. Iodine, nitrogen peroxide and hydrofluoric acid, to mention three examples, all show this phenomenon.

338. A second solid form of sulphur is **monoclinic sulphur**. Again there is no need to worry too much about the exact meaning of the term. This form may be obtained as needle-shaped crystals by heating some sulphur in an evaporating dish and allowing the liquid to solidify. In order to show the crystals it is usual to puncture the solid crust with a knife and to pour off the still liquid sulphur inside. A mass of monoclinic crystals is found under the crust. This form of sulphur is a little lighter specifically than the rhombic (s.g. 1.98) and has a higher melting-point (120°C .). Monoclinic sulphur gradually changes to the rhombic form at ordinary temperatures. If the temperature is kept over 95.6°C . the monoclinic form is stable. The change from rhombic

to monoclinic is, in fact, a change not unlike the ordinary change which occurs in a solid on melting. It is a change from one physical state to another and, like melting or boiling, has a perfectly definite temperature of transition for any given pressure. Such a change may be called a change of "phase". A change of this sort, from one solid phase to another, usually occurs more slowly than a change from solid to liquid or *vice versa*. Thus the change which normally occurs from monoclinic sulphur to rhombic at ordinary temperatures can be compared with the freezing of water on a cold day. Monoclinic sulphur, like rhombic, is soluble in carbon disulphide.

339. If boiling sulphur is suddenly dropped into cold water it solidifies to a brown non-crystalline (i.e. **amorphous**) mass not unlike india-rubber. It is soft and elastic and quite different from the familiar yellow variety. This is a third allotropic modification. It is known as **plastic sulphur**, and is insoluble in carbon disulphide, CS_2 . Under ordinary conditions it gradually hardens but remains insoluble in CS_2 .

340. When sulphur is precipitated in a chemical reaction it frequently—though not always—comes down as a nearly white very fine powder, so fine that it can pass through the pores of a filter paper. Hence it is apt to be a nuisance, as it cannot be removed as simply as most precipitates. This is another amorphous form of sulphur which is soluble in CS_2 . This variety is sometimes known as "milk of sulphur". It may be conveniently made by boiling flowers of sulphur with milk of lime (slaked lime and water) and adding dilute hydrochloric acid, when sulphur is precipitated as a white or very light greenish powder. This form of amorphous sulphur, if left standing for some years, gradually changes to rhombic sulphur. The change is far more rapid if the sulphur is warmed.

Sulphur is a very bad conductor both of heat and of electricity.

341. The element belongs to a natural group with two somewhat rare elements, selenium (Se) and tellurium (Te), and one

very common one, oxygen. This statement will appear a little more reasonable when some of its compounds have been studied. The group may be compared to the halogens. The latter are more famous as a chemical family, not so much because they are more interesting as because they are more easily available. The chemist may go far in his studies without meeting with actual specimens of compounds of tellurium or selenium.

342. Sulphur is an ingredient of gunpowder, perhaps the oldest known explosive. Gunpowder consists of a mixture of sulphur and charcoal with potassium nitrate, or "saltpetre", in the proportion of sulphur 10, charcoal 15, saltpetre 75. The substance is a mixture and it is not important that these quantities should be exact. The chief products on firing the mixture are nitrogen and oxides of carbon, gases, and potassium carbonate and potassium sulphate, solids. The latter are in a finely divided state and form the bulk of the smoke on an explosion of gunpowder. The devastating effect of the action is clearly due to the sudden expansion. The gases liberated occupy, at S.T.P., nearly three hundred times the volume of the original solid powder; in addition much heat is produced by the chemical reaction, thus raising the temperature and tending to increase the volume still further. But if the gases are suddenly released in a confined space there is an abrupt rise in pressure instead and the result is as might be expected. In a typical case it was estimated that the pressure generated was over 40 tons to the square inch.

Gunpowder was known to Roger Bacon (1214-92) and was used for the first time in war at the battle of Crécy (1346). It has been deadly enough in its day, though the devastating action of modern high explosives makes it look almost tame by comparison.

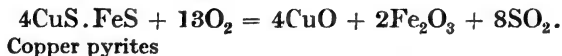
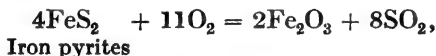
343. Potassium nitrate is soluble in water and sulphur is soluble in carbon disulphide. Hence it will be obvious how gunpowder can be separated into its three ingredients. Note in

passing that *sodium* nitrate is deliquescent and so cannot be kept dry enough for use in gunpowder.

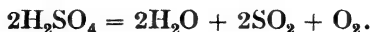
344. Oxides of sulphur. There are at least four oxides of sulphur— S_2O_3 , SO_2 , SO_3 and S_2O_7 —of which SO_2 , sulphur dioxide, and SO_3 , sulphur trioxide, are important substances.

Sulphur dioxide is the familiar gas produced when sulphur is burnt in air. It has a very characteristic pungent smell, to be observed when bad coal or inferior matches are burnt. In the old days before the Metropolitan Railway in London was electrified the smell of sulphur dioxide contributed largely to the unsavoury mixture of gases which made the atmosphere on that line a byword. Yet it was not unhealthy. Sulphur dioxide is a good disinfectant and, if not in excess, its efficiency in killing off germs outweighs its disadvantages as an irritant. It is much used both as a disinfectant and as a preservative.

345. The simplest method of producing the gas is by burning sulphur, as already indicated, or by burning a mineral sulphide in air (see § 671). The latter process, or “roasting”, turns the sulphide to an oxide and is the first stage in the preparation of the free metal:



Sulphur dioxide is also produced in some technical processes by dropping concentrated sulphuric acid on hot bricks:



It can be conveniently produced in the laboratory by the action of a dilute acid upon a sulphite:



(see § 672). This should be compared with the action of a dilute acid on a carbonate. To obtain a good yield of SO_2 a little heating

is necessary as the gas is very soluble in water and so does not come away completely and readily when the mixture is cold. SO_2 can also be produced by heating copper turnings with *concentrated* sulphuric acid (see § 671). This action should be contrasted with the action of *dilute* sulphuric acid on zinc (see § 48). The equation for the action at a temperature above 270° is



This is not the only reaction which occurs, some black copper sulphide, Cu_2S , also being formed. The equation is:



Note that zinc gives SO_2 in the same way with *hot concentrated* sulphuric acid:



Of course so soluble a gas cannot be collected over water. It is much heavier than air and so can be collected in a gas jar, the air being displaced upwards. This must be done in a draught cupboard.

346. Sulphur dioxide, then, is a heavy gas, very soluble in water. The solution is a feeble acid. It also possesses *bleaching* properties, which are as striking as are those of chlorine. Chlorine bleaches because, in the presence of water, it is an oxidising agent. Sulphur dioxide, on the other hand, is a reducing agent. It readily extracts oxygen from bodies and becomes converted into compounds of sulphur trioxide, SO_3 . This is a common explanation of its bleaching properties. The suggestion is that the extraction of oxygen from, say, the colouring matter in a flower converts it to a new substance which is not coloured. This explanation does not seem wholly satisfactory, however, as the colour can frequently be restored by the addition of a strong mineral acid, which would not be the case if it were a simple reduction. Still, SO_2 certainly is a reducing agent, and in some cases this may account for its bleaching properties.

Whatever the exact action may be, chlorine certainly alters the molecule of a colouring matter when it bleaches far more than sulphur dioxide does. The disappointment of a young naturalist who used the fumes of burning sulphur to kill moths for his collection will readily be understood.

347. Sulphur dioxide can easily be liquefied, e.g. by passing it through a U-tube immersed in a mixture of salt and ice. It is liquid at ordinary temperatures at a pressure of three or four atmospheres. This is not a large pressure, and the liquefied gas can conveniently be stored and sold in syphons, just like those in which soda water is usually supplied.

348. The density of sulphur dioxide is 32 ($H = 1$), so its molecular weight is 64. Since the atomic weight of sulphur is 32, there can only be one atom of sulphur to the molecule. This leaves a balance of 32, which must clearly be made up by two atoms of oxygen. Hence the formula is SO_2 .

349. The acid present in a solution of SO_2 is called "sulphurous acid" and is written H_2SO_3 . The salts of this acid are called **sulphites**—"normal sulphites" or merely "sulphites" when both atoms of hydrogen are replaced, and "acid sulphites" or "bisulphites" when only one is replaced. Thus the normal sulphite of sodium is Na_2SO_3 , the acid sulphite or bisulphite is $NaHSO_3$. Acids generally dissolve sulphites with evolution of sulphur dioxide, e.g.



350. Sulphites are much more easily decomposed than are sulphates. If a solution of barium chloride, $BaCl_2$, is added to a solution of sulphur dioxide—i.e. to sulphurous acid—a white precipitate of barium sulphite, $BaSO_3$, readily appears. This precipitate dissolves at once in hydrochloric or nitric acid. But if a solution of sulphur dioxide is left open to the air for a day or two and is then treated with dilute barium chloride solution, the precipitate formed is not entirely soluble in dilute hydrochloric

acid, owing to the presence of some sulphate. Sulphurous acid gradually absorbs oxygen and turns to sulphuric acid, and barium sulphate is a very insoluble substance. The anhydride of sulphuric acid is sulphur trioxide, SO_3 . Thus we have

H_2SO_3
Sulphurous acid

SO_2
Sulphurous anhydride or
sulphur dioxide

H_2SO_4
Sulphuric acid

SO_3
Sulphuric anhydride or
sulphur trioxide

351. Sulphur trioxide, SO_3 . It is very easy to decompose sulphurous acid into the anhydride and water. Gentle heating will effect it, and, indeed, if the solution be strong the decomposition is spontaneous. Sulphurous acid always smells of sulphur dioxide. The decomposition of sulphuric acid into water and sulphur trioxide cannot be effected by any such simple means. The trioxide is made directly by inducing SO_2 to combine with some more oxygen. There is always a slight tendency for SO_2 to pass into SO_3 in the presence of oxygen, but the process is too slow to be of much interest. The gases can, however, be made to react much more rapidly by the use of a suitable catalytic agent, the best known being platinum, and as the effect of the platinum depends upon its surface area it is necessary to arrange for this to be as great as possible. If a piece of asbestos fibre is steeped in a solution of platinum chloride in hydrochloric acid and then heated, the asbestos becomes coated with a thin grey coating of spongy platinum. In this way "platinised asbestos" is produced. If now a mixture of sulphur dioxide and oxygen is passed over heated platinised asbestos, the dioxide is converted into the trioxide, thus:



The apparatus is quite simple and is shown in fig. 35. The vapour of sulphur trioxide which comes off is condensed by means of a freezing mixture into colourless ice-like needles. If

this be stored, without access to moisture, it undergoes some sort of molecular change and turns to a white silky crystalline solid.

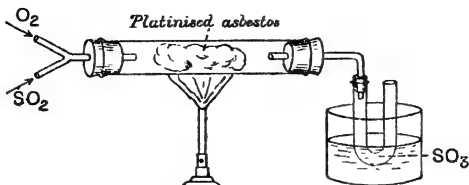
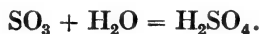


Fig. 35. Preparation of Sulphur Trioxide. (See Plate VI.)

352. Sulphuric acid, H_2SO_4 . Sulphur trioxide combines readily with water, the action being very vigorous, and sulphuric acid is formed:



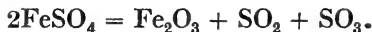
As sulphuric acid is perhaps the most important chemical used, this would appear to be a good way to prepare it. As a matter of fact this method is employed on a large scale and is known as the "contact process", but its introduction is somewhat modern and it is still not the method most widely used, though the reaction has been known for nearly a century. The trouble has been that impurities in the sulphur dioxide tend to "kill" the catalyst. Arsenic is a particularly bad offender and many sources of sulphur certainly contain arsenic, particularly iron pyrites. When the contact process is worked practically, great care is taken to purify the gases as the catalyst is not by any means cheap—platinum is much dearer than gold—and must not be spoilt. More recently a German process has been worked in which mixed oxides of iron and copper are used as a catalyst instead of platinised asbestos. Another process utilising oxides of vanadium as a catalyst has also been very successful. In practice it is usual to pass the SO_3 produced by the contact process into dilute H_2SO_4 rather than into water, as this is found to be more satisfactory. In this way concentrated sulphuric

acid is obtained. If sulphur trioxide is passed in even after the acid is at full strength it continues to be absorbed and fuming sulphuric acid is produced, to which may be assigned the formula $\text{H}_2\text{S}_2\text{O}_7$ (i.e. H_2O , 2SO_3). This used to be called "Nordhausen" sulphuric acid, but now the more serviceable word "oleum" has come into use as a name for this fuming acid.

353. Another process for making sulphuric acid, and a very old one, consists in heating green crystals of ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. If ferrous sulphate is decomposed by heat at all, it might naturally be expected to decompose into the oxide of the metal and the anhydride of sulphuric acid. Consider, for example, what happens when a carbonate is heated. If this were so the action would be

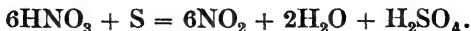


Now ferrous oxide, FeO , is a strong reducing agent, and when it reduces a substance it becomes converted into ferric oxide, Fe_2O_3 . So it is not surprising to find that the decomposition which takes place is represented by the equation



This is what the reaction would become if the first stage, suggested above, actually occurred and then the ferrous oxide reduced half of the sulphur trioxide. The SO_3 produced combines with the water of crystallisation and yields weak sulphuric acid.

354. A simple laboratory method of preparing sulphuric acid consists in boiling sulphur in concentrated nitric acid. Nitric acid has already been described as a strong oxidising agent and it is not surprising that it should oxidise the sulphur, in presence of the water produced by its own decomposition, into sulphuric acid. The main action can be represented thus:



But the reader will by now not expect actions involving concentrated nitric acid and heat to go exactly and entirely according

to the equation. Such actions are rarely "clean". The equation represents the chief reaction and explains how the sulphuric acid comes into being.

355. A process which is much older than the contact process for making sulphuric acid is the "lead chamber" process, which has yielded the bulk of the sulphuric acid, or "oil of vitriol", of commerce for many years and is still far from being ousted by the contact process, though eventually such an event seems not unlikely.

A mixture of water, sulphur dioxide and oxygen (or air) contains all the necessary ingredients of sulphuric acid. The essential feature of the lead chamber process consists in the use of nitric oxide to induce the ingredients to combine. Nitric oxide, we have seen, combines directly and at once with oxygen, forming nitrogen peroxide, NO_2 . Nitrogen peroxide oxidises a mixture of steam and SO_2 to sulphuric acid, being reduced back to nitric oxide again. It is then ready to combine with more oxygen and the process is repeated. The nitric oxide thus acts as a carrier, and, being unchanged at the end, is much like a catalytic agent. The above description gives the essentials of the process. With a deficient supply of steam a crystalline substance called nitrosulphuric acid, $\text{SO}_2 \cdot \text{OH} \cdot \text{NO}_2$, is formed, to be decomposed when more steam is introduced. Some chemists have considered this as an essential stage in the process, but the point is of no particular importance. Others have considered the "carrier" as N_2O_3 .

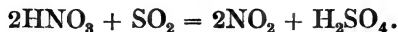
356. Like most chemical processes, when these reactions come to be used on a large commercial scale a number of points become important which do not seem to matter in a description of the theory. In the first place, three of the four oxygen atoms in every molecule of H_2SO_4 are obtained from the air, that is, nearly 49 per cent. by weight of the whole. This is diluted in the air with four times its volume of nitrogen. As the amount of sulphuric acid made by the method runs, literally, into millions of tons

per annum, the volume of air used is, of necessity, enormous. Hence the action is made to take place in very large chambers, usually over 100 ft. long. These chambers are made of lead, which is only slightly acted upon by the acid. The use of big chambers made of metal assists in the removal of the very large quantity of heat carried by the hot gases and produced in the chemical reaction. Commercial oil of vitriol made by this process ordinarily contains a trace of lead sulphate from the chambers.

357. Again, theoretically the nitric oxide should be available for use indefinitely. As a matter of fact there is a fairly large wastage of this gas; some escapes in the gases which pass up the chimney. It will be recollected, moreover, that these actions involving nitric acid and oxides of nitrogen are not simple ones, and in the present case some of the oxides of nitrogen are certainly reduced beyond the nitric oxide stage to nitrous oxide and lost, and some may be reduced to nitrogen. There is so much nitrogen already present from the air that this last point is almost impossible to verify.

358. The more important details of the technical process are as follows. Sulphur dioxide is produced by burning large quantities of iron pyrites, FeS_2 . Before reaching the lead chambers this SO_2 passes along a passage and then up a tower, called a "Glover Tower", the object of which will be seen later. The passage is a long one and as the gases cool somewhat in passing along it, a number of impurities from the pyrites, notably arsenic trioxide, As_2O_3 , are deposited. Notice that the gases here contain a large volume of atmospheric nitrogen which dilutes the reacting gases and hence the necessity referred to above for having the chambers large. On this part of the journey the appropriate quantity of air is introduced into the stream. Nitric acid is also supplied from a heated mixture of nitre and concentrated sulphuric acid. It is not hard to see why this is quite a small part of the apparatus compared to the immense furnaces in which the pyrites is burnt. Note that the oxides of nitrogen

start as nitric acid, which may be regarded as $\text{H}_2\text{O} \cdot \text{N}_2\text{O}_5$. So a first reaction may be assumed to be



From the top of the Glover Tower the mixed gases—all the necessary components except the water—pass into the lead chambers, two or three in succession, into which jets of water in the form of finely divided spray are blown at various points. It was formerly usual to blow in steam instead of water. But the gases are already very hot at this stage, and the added heat caused by blowing in steam is found to be a disadvantage. Sulphuric acid is formed and collects in a rather dilute form—something under 70 per cent., the so-called “chamber acid”—at the bottom and can be run off. If it were not for the tremendous volume of nitrogen mixed with the other gases it might be possible so to adjust the quantities that all the substances were used up without waste, the oxides of nitrogen remaining in the chambers indefinitely. As it is, there must be an outlet to carry off the unwanted nitrogen and, of course, the useful oxides of nitrogen pass off with it. So the issuing gases are passed up another tower—the Gay-Lussac Tower—containing a porous material, usually coke, kept wet with concentrated sulphuric acid, admitted at the top. This acid washes out the valuable oxides of nitrogen. We can now see the utility of the Glover Tower. The acid from the Gay-Lussac Tower is introduced into the Glover Tower at the top. This tower is packed with broken flint-stones over which drips the acid containing the oxides of nitrogen. This acid is referred to in the trade, rather loosely, as “nitrous” sulphuric acid. The sulphur dioxide coming up the tower possesses the property of separating from the sulphuric acid the oxides of nitrogen, which it carries along with it and so these oxides are taken back into the lead chambers. This is the main source of the oxides of nitrogen once the process has been well started, which explains, as the reader has probably already seen for himself, why

the quantity of nitre used is so much less than the quantity of pyrites. The passage of the acid down the Glover Tower concentrates it and it is usual to pass down this tower not only the "nitrous" sulphuric acid but also the chamber acid, the final product of the lead chamber process being drawn not from the chambers but from the base of the Glover Tower. This acid is about 78 per cent. H_2SO_4 and so is more concentrated than the chamber acid; it is from this source that the acid is obtained for use in the Gay-Lussac Tower (see fig. 36).

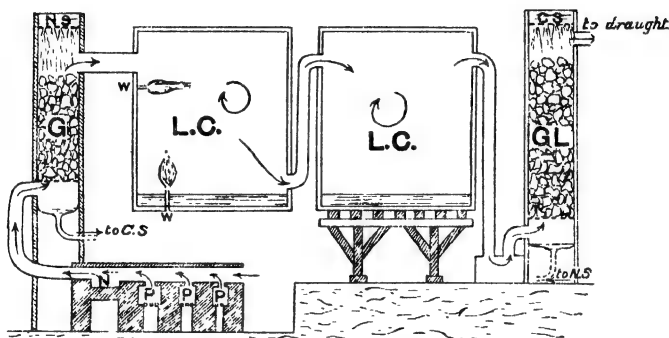


Fig. 36. Preparation of Sulphuric Acid.

359. For many commercial purposes the acid produced by this process is sufficiently concentrated and sufficiently pure. The acid can be purified and concentrated by evaporation under reduced pressure. Such processes are not so simple as they seem, nor are they very cheap. Hence the great advantage of the contact process for providing very concentrated or very pure acid. The acid is sometimes used in processes connected with food-stuffs, and the superiority of the contact method in such cases will be sufficiently obvious.

360. A disadvantage of the lead chamber process arises from the necessarily huge size of the chambers. They are expensive

to erect and take up a large area, so modern improvements tend in the direction of reducing their size. In one modern variety of the plant the lead chambers are replaced by a number of towers, the gases passing through all the towers in series. This secures more rapid and more intimate mixing. In such an arrangement there may be half a dozen towers of which the first is the Glover Tower and the last the Gay-Lussac Tower.

361. In the laboratory, the lead chamber method can be illustrated by delivering SO_2 , steam and HNO_3 vapour into a glass flask, when drops of sulphuric acid collect at the bottom. This does not illustrate, however, the Glover and Gay-Lussac Towers, which are such features of the commercial process. Formerly the acid was prepared without the use of these towers, which made the method much more expensive.

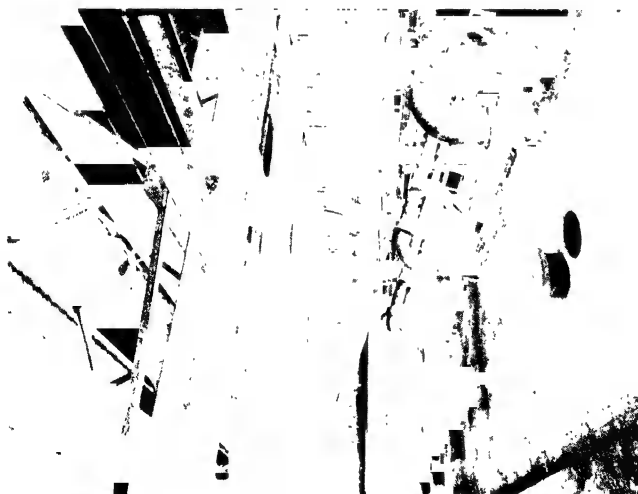
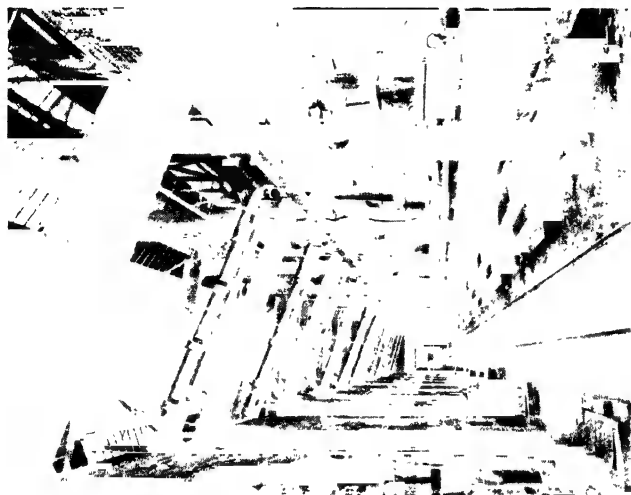
362. Sulphuric acid is a heavy oily liquid. Its density is 1.85 and its boiling-point 290°C. , with decomposition into SO_3 and H_2O . It freezes at 10°C. The vapour density is too small for the formula H_2SO_4 owing to dissociation, and at about 400°C. the vapour density is 24.5, whereas the formula H_2SO_4 leads us to expect it to be 49. Hence the dissociation at this temperature into H_2O and SO_3 appears to be complete. At higher temperatures it is resolved into steam, sulphur dioxide and oxygen.

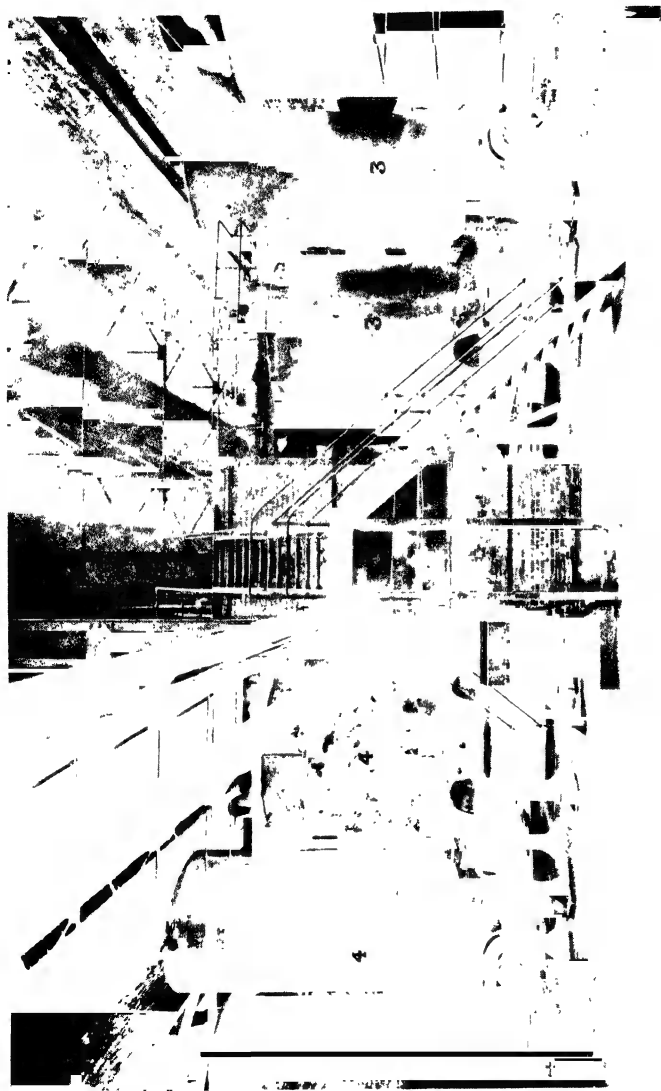
363. Sulphuric acid is a very corrosive liquid. For example, it first stains a black coat red and then burns a hole in it. If a drop of the acid should fall on the coat it must be treated at once with ammonia. We have seen caustic potash used for the purpose, in which case the remedy was just about as bad as the disease. The peculiarly destructive properties of the acid depend largely on the avidity with which it combines with water. A great many organic bodies consist of carbon together with oxygen and hydrogen in the same proportions as in water (see § 321). Examples of this are sugar, starch and cellulose, the last named being the chief ingredient of wood. Though such substances do not actually contain water, the acid treats them just as if the

Manufacture of Nitric Acid.

Right. Overhead, the pipes from the retorts and, on the right, the vertical condensers and receivers.

Left. The tops of the retorts and the holes through which the charges of saltpetre will be poured; also the pipes through which the vapour of the acid escapes.





Manufacture of Sulphuric Acid by the contact process.

The two cylinders marked 3 form part of one unit: those marked 4 another unit. Purified and dried sulphur dioxide and air are heated by passing through tubes in the first cylinder surrounded by the hot gases coming from the second cylinder, which contains the platinum contact. They then pass into the second cylinder where SO_3 is produced and heat is evolved.

oxygen and hydrogen were combined together. Hence they are charred and blackened by concentrated sulphuric acid. Several examples of this have already been met with in chap. xviii. Sulphuric acid is commonly used in the laboratory as a drying agent for gases. Pumice soaked in the acid is especially useful, as a large surface is thus presented to the gas. Or the gas to be dried can be bubbled through the acid. For these purposes the acid must be concentrated.

364. The salts of the acid, the **sulphates**, are usually studied when studying their respective metals. One or two points may be noted here. The three usual insoluble sulphates, BaSO_4 , SrSO_4 and PbSO_4 , have already been mentioned. There are several mineral forms of calcium sulphate—anhydrite, without any water, and selenite, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; also gypsum and alabaster. Plaster of Paris is made by heating the hydrated salt up to about 140°C . This when mixed with water gradually sets into a very hard mass. Curiously enough, if the sulphate be made much hotter than 140°C . it loses its property of setting. Calcium sulphate is slightly soluble in water and is quite interesting and exceptional as being more soluble in cold water than in hot. Barium sulphate is the insoluble white precipitate already referred to in § 350; it is regularly produced when a soluble sulphate is added to a soluble salt of barium. Silver sulphate is somewhat soluble in water; other common sulphates dissolve freely. The reader should here refer back to the latter part of chap. xv.

365. A number of double sulphates are of interest. For example, nickel ammonium sulphate, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, is worth notice as it is much used in nickel electroplating. There is, too, the interesting class of the **alums**, of which common alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is a typical member (see chap. xxxv).

366. **Sulphuretted hydrogen**, H_2S , can be prepared directly by passing hydrogen through boiling sulphur, or by burning a jet of hydrogen in sulphur vapour. It is more conveniently

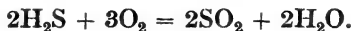
prepared by acting on ferrous sulphide with a dilute acid (see § 677). Ferrous sulphide can be made directly by heating an intimate mixture of sulphur and iron filings:



A number of other sulphides serve the purpose equally well. For a purer product it is convenient to use the sulphide of antimony, Sb_2S_3 . In this case heating is necessary.

367. Sulphuretted hydrogen is a gas and is evolved by the action of hydrochloric acid on ferrous sulphide without heating. It is frequently made in Kipp's apparatus, described in § 48. This is especially convenient as the gas is of great use as a reagent, and by using this apparatus it is always ready to hand. The gas is soluble in water and mercury is not unaffected by it. The gas is a little heavier than air and can be collected in a jar by displacing the air upwards; or it can be collected over *hot* water. At normal temperatures water takes up about three times its volume of the gas. It is far more soluble in alcohol.

368. The most obvious thing about the gas is its odour, the odour of rotten eggs already referred to. The gas burns readily in air, thus:

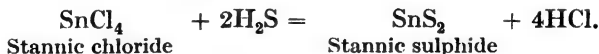
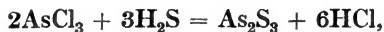
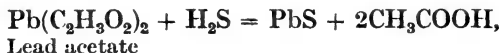


The flame is pale blue, like that of sulphur but less luminous. With a deficient air supply sulphur is deposited. A solution of the gas is faintly acid, and hence the alternative name "hydro-sulphuric acid". A comparison with the halogen acids will justify its title. It is exceedingly useful in analysis. When passed into a solution containing a metal it frequently gives a precipitate of the **sulphide**, and the colour and condition of deposit are often of great assistance in identifying the metal (see § 702). When passed into a solution of KOH or Ba(OH)_2 a solution of the sulphhydrate, KHS or Ba(SH)_2 , is formed.

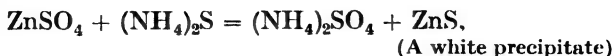
369. When sulphuretted hydrogen is used for testing a solution for the presence of certain metals the solution is first acidified

with dilute HCl and then gaseous H_2S is passed in—usually from a Kipp's apparatus.

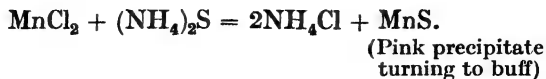
Of the salts of the common metals in solution the following give with H_2S sulphides which come down as precipitates: salts of lead, bismuth and copper and mercuric salts all give black precipitates. As lead gives a white precipitate with HCl, it can easily be distinguished from the other three. The precipitated sulphides of bismuth and copper are much alike. In the case of mercury the precipitate is at first yellow, turning rapidly red and then black. Arsenic yields a yellow sulphide. So does cadmium, but care *must* be taken that the HCl present is dilute. Cadmium sulphide, CdS , is soluble in moderately strong HCl. Tin also yields sulphides in the same way. Stannous salts yield a brown precipitate, SnS , and stannic salts a yellow precipitate, SnS_2 . This last is not so vivid a yellow as sulphides of arsenic or cadmium. Antimony yields an orange sulphide. The student should certainly go through the process of making all these sulphides for himself and should note their appearance carefully. The equations are all just as would be expected from the valencies of the metals. Three typical ones are



370. It will be noticed that each of these reactions yield HCl as well as the sulphide, so that if the sulphide is at all soluble in HCl there is a tendency for the reverse action to take place and little or no precipitate is obtained. In such cases the sulphide may often be obtained by adding ammonium sulphide, $(\text{NH}_4)_2\text{S}$, in solution instead of H_2S . For example, in the case of zinc the equation is

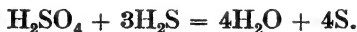


and in the case of manganese it is



Neither of these sulphides would be precipitated from an acid solution, even if the acid were dilute.

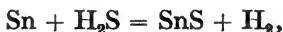
371. When dry H_2S is required, it will be clear that it cannot be dried by a basic drying agent such as KOH . It has been seen that in such a case a sulphide or hydrosulphide would be formed. Nor can sulphuric acid be used. H_2S is a reducing agent, and with concentrated sulphuric acid it yields sulphur, thus:



Calcium chloride, however, is quite satisfactory as a drying agent for H_2S (contrast with ammonia, § 286).

372. The density 17 ($H = 1$) and a knowledge of the fact that the gas contains sulphur and hydrogen and nothing else supply sufficient data to settle the formula. From the density, the molecular weight is 34. Hence there cannot be more than one atom of sulphur to the molecule. Two atoms would require the density to be more than 64. So there is one atom of sulphur and the balance must be accounted for by two atoms of hydrogen. So the formula is H_2S .

If a piece of tin or cadmium is heated in sulphuretted hydrogen the action is



or



By using a definite quantity of the gas in a closed tube it can be shown that the volume of hydrogen liberated is the same as that of the sulphuretted hydrogen used. This confirms the H_2 in the formula.

373. Carbon disulphide. One other compound of sulphur demands our attention for a moment. When sulphur vapour is passed over red-hot carbon, direct union takes place and there is

produced carbon disulphide, CS_2 , the volatile liquid already referred to as a solvent for sulphur and for the halogens. The crude compound smells like bad cabbages, but this is not the smell of the pure substance. Carbon disulphide readily burns with a blue flame and the vapour mixed with air is highly explosive. The liquid is a very valuable solvent. It dissolves gutta-percha, india-rubber and many other organic substances, and is used in technical processes for extracting scent from flowers and for other similar purposes.

374. It has been mentioned that sulphur belongs to the same group of elements as oxygen. This may best be seen by comparing the formulae of a number of their compounds. There are a large number of oxides and sulphides of similar composition, e.g. H_2O and H_2S , H_2O_2 and H_2S_2 , FeO and FeS , Sb_2O_3 and Sb_2S_3 , CO_2 and CS_2 and many others. The sulphydrates, NaSH , etc., can be compared to the hydroxides, NaOH , etc., and in organic chemistry the "mercaptans" are a large class of bodies which contain the group SH where the alcohols contain OH , e.g. ordinary alcohol is $\text{C}_2\text{H}_5\text{OH}$ and the corresponding mercaptan is $\text{C}_2\text{H}_5\text{SH}$. Ammonium cyanate is NH_4CNO , ammonium thiocyanate (or sulphocyanide) is NH_4CNS . The number of oxygen and sulphur compounds which can be paired in this way is very large and fully justifies classing oxygen and sulphur together chemically, although viewed physically they appear so different.

Chapter XXV

PHOSPHORUS AND ITS COMPOUNDS

375. Phosphorus has been referred to from time to time in our work, and anyone who has seen the vigorous way in which it burns in oxygen and has noted the almost mysterious caution with which it has to be handled cannot fail to feel curious to learn more about it. But it will at this stage be a matter of no surprise to learn that this exceedingly active substance exists in nature in compounds of a most innocuous and unexciting type.

376. There are two main sources of phosphorus. First, there are in the mineral world a number of phosphates, of which calcium phosphate is by far the commonest. This is a most important mineral, phosphates being essential to the farmer in some important kinds of manure. The little Island of Nauru, a mere spot on the map which might be expected to be hardly worth considering, is possessed jointly by the United Kingdom, Australia and New Zealand, its claim to notice resting entirely upon the phosphates it contains; its export is over 300,000 tons a year. Christmas Island, also quite small, supplies annually over 100,000 tons. Another interesting mineral containing a phosphate is apatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$.

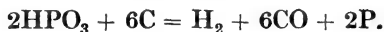
377. There is a second and quite different source of phosphates, and that is bone. Bones consist of an intimate mixture of calcium phosphate and organic matter, either of which may be removed without destroying the form of the bone. Hydrochloric acid dissolves the phosphate and leaves the bone quite soft and flexible. It is the phosphate which is responsible for its hardness. Or the organic matter may be burnt away. If this is only partially effected a great deal of carbon remains and we

have bone-black (see § 216). If the carbon is completely burnt away a white amorphous ash of calcium phosphate remains.

378. There are two common ways of preparing phosphorus from a phosphate, which are not really so different as they look, the principle in both cases being reduction by carbon. In the older method calcium phosphate is treated with concentrated sulphuric acid, when the action is

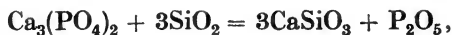


The insoluble calcium sulphate is easily separated from the liquid phosphoric acid and the latter is then heated strongly with carbon. Phosphorus is liberated, and as it melts at 44°C . and boils at 287°C . it can easily be distilled off, provided that air is excluded:



The vapour is cast into sticks under water; it is far too inflammable to be allowed to come into contact with the air.

379. The modern method consists in heating in an electric furnace an intimate mixture of coke, calcium phosphate and silica, the latter being in the form of sand. If the silica, SiO_2 , is regarded as the anhydride of silicic acid, this method is effectively the same as the other, using the silicic anhydride instead of the sulphuric acid and working the two stages of the process together:



The calcium silicate melts at the high temperature of the furnace and is run off at intervals at the bottom, a further charge of phosphate, silica and carbon being introduced at the top. The phosphorus is distilled off, air being excluded. Notice carefully that the sole use of the electric current is to produce great heat. The method is not an electric one in the sense that, for example, the splitting up of water in a voltameter is. This

reaction, used here for producing phosphorus, should be carefully compared with the cases of electrolysis which will be described in chap. XXIX. On the other hand, the production of nitric oxide directly from its elements resembles the method of preparing phosphorus, as in both cases the electric current is used only for heating. The reader should be careful not to confuse these two quite distinct uses of an electric current.

380. Phosphorus produced in this way is a white or light yellow waxy solid which readily burns with a very bright white flame. In air it glows in the dark with a characteristic "phosphorescence" due to slow oxidation. Note, however, that the word "phosphorescence" is used to describe a light of this sort, even when it has nothing to do with phosphorus, such as the light of a fire-fly or glow-worm or the beautiful phosphorescence so often to be seen in sea water.

381. White phosphorus and red phosphorus. Phosphorus exists in at least two distinct allotropic forms—"white" phosphorus, described above, and "red" phosphorus. Whereas white phosphorus is a very active substance, red phosphorus is comparatively inert. The change from white to red is effected by heating phosphorus to about 250°C . with a trace of iodine as a catalyst. Heat is evolved during the change. This is an important commercial operation, red phosphorus being made in great quantities for use in the manufacture of matches. Any unchanged white phosphorus is easily removed. It is soluble in carbon disulphide or it can, more cheaply, be destroyed by boiling with caustic soda; neither carbon disulphide nor caustic soda affects red phosphorus.

382. Since white phosphorus gives out heat when it is converted into red, it follows that red phosphorus must give out less heat per gramme than white when completely burnt, as each burns to the same oxide. Hence a gramme of white phosphorus possesses more chemical energy than a gramme of red, which would account for its greater activity.

383. It is usual to compare the two forms of phosphorus, but as a matter of fact it would be hard to find any single point worth mentioning in which they resemble each other—white phosphorus, a white, waxy, highly inflammable, very active, very poisonous solid with a low melting-point, insoluble in water but easily soluble in carbon disulphide, ether, benzene and many other liquids; and red phosphorus, a red crystalline substance (though the crystals are very small) which does not catch fire till heated to about 260°C ., not very active, not at all poisonous, insoluble in water, it is true, but insoluble, too, in all the ordinary solvents which dissolve white phosphorus. Nevertheless, the compound formed by burning a gramme of red phosphorus is identical, both in quality and quantity, with that formed from a gramme of white, and it is this fact which proves that they are two different forms of one and the same element.

384. Phosphorus as an element has two uses. It is employed, mixed with flour or some other like food-stuff, as a poison for vermin, notably rats. Also, and this is far more important, it is used for making matches.

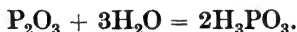
385. The composition of the head of a match contains three kinds of ingredients: (1) something readily oxidisable, (2) an effective oxidising agent, (3) some sort of binding material. Matches formerly contained white phosphorus under (1), but as this made them dangerously inflammable and the phosphorus was also very poisonous to the workers in the match industry, it is now forbidden by law in most civilised countries. It is replaced by phosphorus sulphide, P_4S_3 , or by a form of phosphorus, scarlet phosphorus, which has most of the advantages of red phosphorus, but is somewhat more easily inflammable. "Safety" matches, which "strike only on the box", contain sulphide of antimony but no phosphorus. There is, however, red phosphorus on the box, together with antimony sulphide, mixed with powdered glass.

The oxidising material in matches is usually potassium

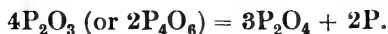
chlorate and red lead (Pb_3O_4), mixed. Potassium nitrate is sometimes used for the purpose. The binding material is for the most part glue. An explanation sometimes given of the working of a safety match is that the friction turns a little of the red phosphorus on the box to white phosphorus, which then burns and sets fire to the match. This, however, is difficult to verify. In non-safety matches the head is sufficiently inflammable to be ignited by the heat of friction on any rough surface.

386. Oxides of phosphorus have been described having the formulae P_4O , P_2O_3 , P_2O_4 and P_2O_5 . Of them the second and fourth are of importance and must claim our attention in some detail.

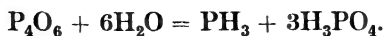
Phosphorus trioxide, often written P_2O_3 , is, in the vapour state, correctly represented by P_4O_6 . As the molecular formula of the solid is not known, the formula P_2O_3 will serve well enough (see § 119). It is formed when phosphorus is burnt with limited supply of oxygen. Compare this with the formation of a carbon monoxide. Like that substance, it is unsaturated and is readily oxidised, when it is converted to the pentoxide, P_2O_5 . The trioxide is more easily volatilised than the pentoxide, and so may be separated from a mixture of the two by gently heating without access to air, and condensing the vapour given off. It dissolves in cold water to give phosphorous acid:



P_2O_3 is a reducing agent and a somewhat strong one. In fact, under some circumstances, the molecules act upon each other, some reducing the others. Thus, when heated in a sealed tube the action is



When dissolved in hot water the reduction and oxidation go farther, the main reaction being



Other reactions occur at the same time, a deposit of red phosphorus being formed, showing that the reduction to PH_3 is not complete. This is a good example of a reduction which in the first stages is a removal of oxygen and in the later stages is an addition of hydrogen.

387. The trioxide readily burns in air or oxygen, forming the pentoxide; the flame is very bright. The trioxide combines readily when heated with sulphur, giving a compound $\text{P}_4\text{O}_6\text{S}_4$. This should be read in conjunction with § 374, where oxygen was compared with sulphur.

388. Phosphorus pentoxide, P_2O_5 . The usual method of preparing the pentoxide, P_2O_5 , is by burning phosphorus with plenty of oxygen. The vapour of this oxide requires the formula P_4O_{10} ; the chemist, while not forgetting this, usually employs the simpler formula P_2O_5 for the solid, just as he does for the trioxide. The pentoxide combines vigorously with water, hissing and giving out much heat. Compare this with the action on water of SO_3 . The action with cold water produces metaphosphoric acid, HPO_3 :



On boiling, this is converted into orthophosphoric acid, H_3PO_4 :

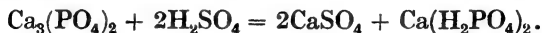


389. Phosphorus pentoxide is one of the most powerful dehydrating agents known. This is because it combines with water to form a stable compound, HPO_3 . Calcium chloride and sulphuric acid form compounds with water which are not so stable and cannot dry a gas completely.

390. Phosphates. The more familiar salts of the acids of phosphorus are salts of orthophosphoric acid. The acid is tri-basic and so there are three sodium salts: NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 . Of these the first is acid, and the second slightly alkaline and the third very alkaline to litmus. It is the second

salt, Na_2HPO_4 , which is usually referred to as "sodium phosphate". It is an effective "pick-me-up" and, even before the advent of prohibition, was much used in the drinks supplied at the "American Soda Fountain". The "American Soda Fountain" is a common feature of fairs and places of amusement, even in this country.

391. Phosphates, it has been mentioned, are of great importance to the farmer, but mineral calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is too insoluble to be useful as a manure. When heated with the right proportion of sulphuric acid the action is



The acid calcium phosphate thus formed—also called "superphosphate"—is sufficiently soluble in water to be absorbed by plants. Phosphate manure usually consists of this mixture of calcium sulphate and superphosphate.

392. When phosphoric acid is heated it is converted first to pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, and then to metaphosphoric acid:



Phosphoric acid is also formed when red phosphorus is heated with strong nitric acid, and this is a very handy laboratory method.

393. It is important to note that if sulphuric acid is mixed with a phosphate and the mixture distilled, it is sulphuric acid and not phosphoric acid which comes over in the distillate. This should be contrasted with the action of sulphuric acid on nitrates and chlorides. On the other hand, if phosphoric acid is distilled with a sulphate, again it is sulphuric acid which is distilled off. Similar results would be obtained if chlorides or nitrates were heated with phosphoric acid.

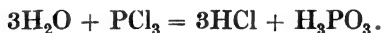
394. If phosphoric acid is concentrated by steady heating, it eventually reaches a stage at which the liquid deposits on

cooling crystals of the pure acid. These crystals melt at about $40^{\circ}\text{C}.$, so that pure phosphoric acid is at ordinary temperatures a solid.

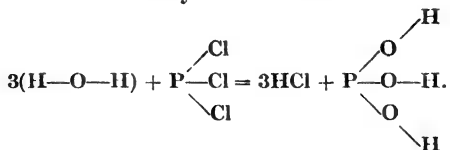
395. All phosphates give a characteristic yellow precipitate when warmed (not boiled) with plenty of strong nitric acid and a solution of ammonium molybdate. The silver salts of ortho-, pyro-, and metaphosphoric acid are deposited when a solution of silver nitrate is added to a solution of the phosphate. The orthophosphate is yellow and the other two white. Metaphosphoric acid possesses the power of causing albumen to solidify, which the other phosphoric acids have not. In practice this means that when a solution containing metaphosphoric acid is added to white of egg it clots, much as if it had been boiled.

396. Chlorides of phosphorus. Phosphorus forms two chlorides, phosphorus trichloride, PCl_3 , and phosphorus pentachloride, PCl_5 . The trichloride, a liquid, is produced when chlorine is passed through melted phosphorus without access to air. The trichloride distills over. On exposing this liquid to more chlorine it combines with more of the gas and yields solid crystals of the pentachloride.

397. Phosphorus trichloride acts upon water and gives phosphorous acid:

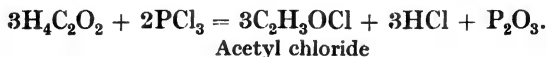


If we write this structurally it becomes

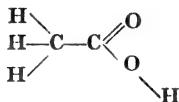


This may be described by saying that the chlorine has replaced the "OH group" in the water. This OH group, or radical, is often called "hydroxyl", and it is found in many other substances besides water. The detection of hydroxyl groups is a

common use of the chlorides of phosphorus. If a substance contains an atom of oxygen and one of hydrogen in the molecule, and by the action of a chloride of phosphorus *both* are removed and replaced by *one atom* of chlorine, it is strong evidence that the atoms of oxygen and hydrogen form a hydroxyl group. For example, the formula of acetic acid is $\text{H}_4\text{C}_2\text{O}_2$. When it is gently warmed with PCl_3 the action is

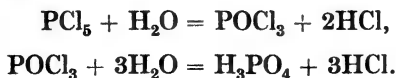


Here an atom of chlorine has displaced an atom of oxygen and one of hydrogen. So the acid may be written $\text{H}_3\text{C}_2\text{O}.\text{OH}$. This is the first stage in finding out how the atoms in a molecule of acetic acid are linked up. The full formula eventually turns out to be CH_3COOH or



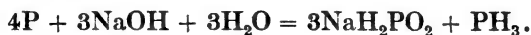
(see §§ 249 and 251). This agrees well with a fact that has already been noticed, namely, that the acid is monobasic. It will be noticed how clearly the formula brings out that one atom of hydrogen is placed quite differently to the other three.

398. Phosphorus pentachloride reacts with water forming phosphoric acid, with an oxychloride as the product at an intermediate stage:



399. Phosphine, PH_3 . There remains for our present attention one further compound of phosphorus, phosphorus trihydride or phosphine, PH_3 . This has already been referred to in connection with the action of P_2O_3 on *hot* water. It is more usually prepared by heating yellow phosphorus in a solution of caustic

soda, without access of air. This is conveniently done in a retort as for the preparation of nitric acid (see fig. 34). The outlet of the retort passes into a trough of water and the gas is collected in a gas jar, using a beehive shelf in the usual way. The air must first be driven out by nitrogen, coal gas or any other suitable gas which does not act upon the phosphine. Phosphine is poisonous; it has, too, a very disagreeable odour, the odour of decaying fish, and it must be prepared in the draught cupboard. The equation is

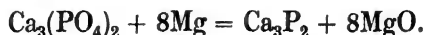


This is by no means the only reaction which occurs. A large amount of free hydrogen is produced and also traces of another hydride of phosphorus, P_2H_4 . This latter impurity causes the phosphine to be "spontaneously inflammable" in the air; that is, it catches fire of itself without being lit. It is this fact which makes it necessary to drive the air out of the apparatus before preparing the gas. It is a common lecture experiment to bubble the phosphine through water into the air, and each bubble as it comes to the surface burns at once to give a ring of white smoke. These rings are curiously perfect in their shape, and the effect, as they ascend in rapid succession, getting larger as they rise, is most striking. The hydride, P_2H_4 , has the property of making many other combustible gases spontaneously inflammable, when the P_2H_4 is present even in small quantities.

400. The formula PH_3 at once recalls that of ammonia, from which, however, phosphine differs considerably. It is not, for example, appreciably soluble in water. Again, PH_3 gives no alkaline reaction with water. It does, however, combine with HCl and with HI to form PH_4Cl , phosphonium chloride, and PH_4I , phosphonium iodide. The chloride can only be made with difficulty under pressure, but the iodide is fairly stable under ordinary conditions. With KOH it readily yields phosphine, which recalls a similar reaction between KOH and an ammonium

salt. The phosphine prepared in this way is not spontaneously inflammable.

Phosphine can also be prepared by the action of water on a phosphide. If a phosphate is heated strongly with powdered magnesium it is reduced to a phosphide:



Calcium phosphide is made commercially by heating the phosphate with carbon in an electric furnace, but magnesium reduces the phosphate more readily and at a lower temperature. In the laboratory the phosphide is easily made by mixing the magnesium and the phosphate and heating them in a small hard-glass tube. A phosphide and water yields phosphine even in the cold:



This phosphine is spontaneously inflammable. By adding a little water to the contents of the hard-glass tube after heating, the phosphine is detected both by its smell and by the way it at once takes fire. This provides a simple and convenient test for a phosphate, additional to those already mentioned.

401. The reaction between a phosphide and water should be compared with the action of water on the carbides of aluminium and calcium referred to in chap. XIX. A mixture of calcium carbide with a little calcium phosphide yields with water spontaneously inflammable acetylene. This is the basis of a method of making flares at sea. The mixture of carbide and phosphide is placed in a perforated tin container and attached to a float. The sea water liberates the gases, which at once take fire and burn with a brilliant light. These flares are called "Holmes' signals", after their inventor.



Crystallising Washing Soda. Notice the size of the crystallising pans.



Refining Silver by Electrolysis.

A thin plate of pure silver is used as the kathode, on which more silver is deposited as the current flows; at the same time silver is dissolved from a block of impure metal, forming the anode. Copper can be refined in a similar manner.

Chapter XXVI

SILICON AND BORON

402. There are two other non-metals that the chemist should know something about at this stage, silicon and boron.

Silicon. Oxygen is the most abundant element in nature, forming as it does nearly half the total weight of the earth's crust. Silicon accounts for about half the remainder. We cannot assume that the inside of the earth, of which we know so little, resembles in composition the outside, with which we are tolerably familiar. For one thing, the density of the whole earth is much greater than the density of the outside crust, and so, presumably, the heavier elements are commoner as we descend. There may be depths at which gold, for instance, is quite plentiful. Still, in the world as far as it is at the chemist's disposal for investigation, silicon is exceedingly abundant and its oxide, silica, constitutes 60 per cent. of the earth's crust. Oxygen may be described as the king of elements, with carbon as his chief officer in the organic world, the world of living things, and silicon as his chief lieutenant in the inorganic world, the world of earth and rock. Carbon gets its full share of a chemist's attention; the study of its compounds is unending. It is, therefore, somewhat surprising that silicon is so frequently passed over in comparative silence.

There are several reasons for this. In the first place, most of the compounds of silicon are solids, and insoluble solids at that. Gases and liquids are in many ways easier to deal with than solids. The numerous reagents employed by the chemist for testing things are usually liquids, often solutions, simply because liquids are convenient to use and frequently react at once. Silicon compounds are thus not used more than necessary.

Again, there are no important energy changes associated with compounds of silicon; it forms an essential ingredient of no foods and of no fuels. However, as silicon compounds do such an amazingly useful service as to provide the bulk of the dry land on which we go about our avocations, we have no right to complain if we get no further service from them. Indeed nearly the whole of the material background of nature consists of compounds of silicon, with the important exception of such parts as are of chalk or limestone. Silicon provides the canvas upon which natural scenery is painted. And it can go farther. When there is no organic life to paint the picture, the compounds of silicon can go a long way to provide a landscape without it. In that case they are usually aided by iron, iron compounds forming the chief colouring matter of the mineral world (see § 571).

403. Silicon compounds do serve for two important everyday uses.

In the first place they provide a variety of excellent building stones. These include the various kinds of sandstones—oolite, Bath stone, Portland stone and the like, which are mainly silica, SiO_2 , cemented together by calcium carbonate—and also granite and syenite. Granite is a mixture. It contains silica as *quartz*, and also different kinds of mica and felspar, both of which are complicated silicates of aluminium and potassium (more rarely sodium), with iron and other metals present in varying quantities. Syenite is similar to granite but with less silica present. Note that marble is a variety of CaCO_3 and does *not* contain silicon.

In the second place they provide us with glassware and pottery. So though the element may provide little of purely chemical interest and so its importance may be obscured, yet it serves as a good illustration of the fact that so very much of the world's most important work is done by the obscure and unrecognised worker. Silicon is essentially a "son of Martha", humdrum and efficient.

404. Silicon dioxide or silica. The simplest compound of silicon is the oxide SiO_2 , and this is its only known oxide. It exists in nature very commonly as sand and more rarely as quartz, flint and several rarer minerals. Silicon dioxide or silica is white when pure, though natural sands are usually yellow from a trace of iron. From the dioxide silicon can be made by reducing it with magnesium at a considerable temperature, or, in the great heat available in the electric furnace, carbon may be used to effect the reduction. Both crystalline and amorphous forms of the element are known. It is not an important substance and it is not very active chemically. It burns in air or oxygen to give the dioxide.

405. There is no need to tell the reader that sand—silica—is practically insoluble in water. Now the formula of silica is SiO_2 and from a consideration of this formula and that of water we might expect to be able to prepare acids such as H_2SiO_3 or perhaps H_4SiO_4 . It is not certain that these compounds exist, though a jelly-like substance containing silica and a variable quantity of water can be prepared. Its formula may be written $\text{SiO}_2 \cdot x\text{H}_2\text{O}$.

Silicates, with formulae such as Na_2SiO_3 , CaSiO_3 and BaSiO_3 , can be prepared in a crystalline form; but great difficulty is encountered in assigning such simple formulae to the naturally occurring mineral silicates. In some instances the mineral consists of a definite compound, e.g. potash-felspar, KAlSi_3O_8 , but in most others it is a mixture of several compounds, and its composition cannot be represented by any ordinary chemical formula. The number and variety of silicates is legion. Any book on minerals teems with them—felspar, augite, serpentine, kaolin, asbestos and so on *ad nauseam*. Their formulae are of necessity somewhat disconcerting in their complexity. They are usually simpler if written as compounds of a metallic oxide, silica and water. China clay, for example, which is one of the simpler ones, is written $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

406. Silica when fused with caustic soda or with sodium carbonate yields a silicate soluble in water which may be written $\text{Na}_2\text{O} \cdot \text{SiO}_2$ and which corresponds to an acid H_2SiO_3 . When a solution of this silicate is treated with hydrochloric acid a gclatinous precipitate is deposited which is the compound of silica and water of indefinite composition already referred to. On heating this strongly pure silica is obtained as a white insoluble powder.

407. Sodium silicate has a commercial use as a preservative; it is sold as "water glass". Eggs kept in the solution are preserved from decay, as the pores in the shell are clogged up and no air can penetrate to rot the egg. Water glass also has a limited use as a preservative for old woodwork.

408. This soluble silicate is obviously of no use as glass in the ordinary sense. Glass as commonly known is a mixed silicate, obtained by heating sand strongly with some carbonate or carbonates other than pure sodium carbonate. The cheaper kinds are a double silicate of sodium and calcium, formed by heating the mixed carbonates of sodium and calcium with plenty of sand. This glass is easily melted in a flame. The hard glass, familiar in much chemical apparatus, is made by using potassium carbonate, instead of sodium carbonate, as this is found to give a far less fusible product. Much modern hard glass consists of boro-silicates; boracic acid is one of its constituents. Flint glass contains silicate of lead, lead oxide being used in place of calcium carbonate in its manufacture. Much use is now made of pure silica as a substitute for glass. This has become possible in recent years owing to the introduction of much improved methods for using very high temperatures. This "fused quartz" ware changes very little in size on heating, and the way it can stand sudden cooling is in very pleasing contrast to the habits of ordinary glass. The cracking of a piece of glass apparatus owing to injudiciously sudden cooling is a painfully familiar accident. When glass is manufactured it

always has to be cooled slowly. Otherwise it is exceedingly brittle, and if it does not break in the making it is very liable to do so at any time after. Such glass could only be used for articles of poor quality.

409. Silicon forms an interesting fluoride, SiF_4 , which is a heavy gas. Its method of preparation has been mentioned in § 203. The hydride, SiH_4 , is also known. It is spontaneously inflammable in air.

410. Boron. Boron is of interest as it occurs in **boracic** (or boric) **acid** and in **borax**. The element itself may be obtained, like silicon, by reducing the oxide B_2O_3 with magnesium or carbon at a suitably high temperature. Borax or tincal, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is the most important naturally occurring compound of boron. It occurs in certain natural hot springs in Italy and in the borax lakes of the U.S.A. Calcium and magnesium borates are also found as minerals in South America and in California. If concentrated sulphuric acid is added gradually to a strong solution of borax in water, boric acid, H_3BO_3 , crystallises out on cooling, as it is far less soluble than either borax or sodium hydrogen sulphate:



Not all the boric acid is precipitated, as the compound is somewhat soluble in water. The yield is in the form of small glossy scales.

The chief source of boric acid is the calcium borate referred to above. The powdered borate, $\text{Ca}_2\text{B}_6\text{O}_{11}$ (or $2\text{CaO} \cdot 3\text{B}_2\text{O}_3$), is mixed with boiling water and sulphur dioxide is passed through the liquid. Calcium sulphite is formed in solution and the boric acid is crystallised out:



Boric acid on heating strongly is converted to the oxide and water:



Great heat is necessary to expel the last traces of water. The oxide is hygroscopic, that is, it readily absorbs moisture from the air.

411. Borax and boracic acid are employed as very mild antiseptics. Boracic acid is also used as a preservative for cream, etc. There is some difference among scientists as to how far boracic acid does harm when taken in this way with food. The danger is considered sufficiently great for the authorities to make strict rules as to its use.

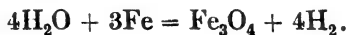
412. Boric acid is a very feeble acid, and the salt borax is, in solution, strongly alkaline. The reason for this will be understood after reading § 458.

413. A small piece of borax heated in a loop on the end of a platinum wire in the Bunsen flame melts and yields a glassy mass. Many metallic salts when heated with such a "borax bead" give definite colours and these colours are used in testing for the metals (see § 696 and onwards).

Chapter XXVII

REVERSIBLE ACTIONS, BALANCED ACTIONS AND DISSOCIATION

414. Anyone who has read chap. v will feel justified in saying "Steam acts upon red-hot iron to produce hydrogen". This is true. The equation is usually written



If now the oxide Fe_3O_4 be placed in a tube and heated to redness while a stream of hydrogen is passed down the tube, the opposite reaction takes place:



At a first glance these two facts appear bewildering. They seem to contradict each other. To reconcile them, consider a third case. Suppose some iron filings are heated in steam and the steam and the products of the action are *allowed to remain* together. Suppose, further, there is enough iron to reduce all the steam. If the first action mentioned above took place completely, all the steam would disappear and be replaced by hydrogen. But if this happened, clearly the reverse action would take place, the hydrogen would reduce the oxide. It is not difficult to guess what actually does happen. Some of the steam is reduced to hydrogen and this hydrogen at once starts the reverse action, the reduction of the oxide. At first this reverse action is slight, but as the hydrogen accumulates it becomes more pronounced until a stage is reached when the two opposite tendencies *balance*. It is not supposed that at this stage all action ceases. The oxidation and reduction probably both continue, but at the same rate. Thus the amount of the oxide present does not change, but any particular atom of iron may be sometimes free and sometimes in a

molecule of oxide. So also any atom of hydrogen may sometimes be in a molecule of H_2 and sometimes in one of H_2O . There is a state of *chemical equilibrium*. When the action of steam on red-hot iron is used as a source of hydrogen (as in chap. v), the hydrogen produced is removed as fast as it is made. Hence the reverse action gets practically no chance of taking place. Similarly when hydrogen is passed over the oxide it is the steam produced which is removed.

415. If the reader has followed this carefully he will no longer be puzzled by the seeming contradiction of the two cases. This example also calls attention to a very important point, namely, that a *chemical action* is not determined merely by the chemical properties of the substances involved but *may be largely controlled by the conditions of the experiment*.

416. Looked at merely as if it were an equation in algebra, *any* chemical equation will clearly balance if the two sides are interchanged. As a matter of actual fact in the majority of cases the reversed equation obtained in this way does not represent any actual chemical event. For example, if iron filings are exposed to moist air, the reaction which occurs is represented by the equation

$$4Fe + 6H_2O + 3O_2 = 4Fe(OH)_3.$$

But there appears to be no ordinary set of conditions under which ferric hydroxide splits up into iron, water and oxygen. If such an action be possible at all it can only be under very special circumstances.

417. On the other hand, there are quite a number of actions which *do* work both ways. In such cases if all the products of the reaction are allowed to remain together a balance-point is reached in which neither the forward action nor the reverse action is complete. But commonly one at least of the products of a chemical action is removed from the arena and this prevents the reverse action, so that the forward action is completed. This has been illustrated by the case of red-hot iron and steam.

Another good example is the heating of chalk, CaCO_3 . In the ordinary way the action is



This is the usual method of making lime, the CO_2 being allowed to escape (see §§ 229, 230). But limewater, we know, can combine with CO_2 ; and quicklime, CaO , can absorb CO_2 , even when hot. If the calcium carbonate be heated in a *closed* space, so that no CO_2 escapes, the pressure of the CO_2 evolved increases until *either* all the carbonate is decomposed *or* a pressure is reached at which the action stops. Which will occur will depend upon the size of the vessel. The increased pressure of CO_2 aids the reverse action until eventually the two actions balance. On the other hand if lime be heated in a closed space containing CO_2 at a sufficiently high pressure the lime begins to absorb the CO_2 , so reducing the pressure. This decreases the tendency of the lime to absorb the CO_2 until, at a certain pressure depending on the temperature, the decomposition of the CaCO_3 , due to the heat, goes on as fast as the absorption, when the action stops. Of course, if there is not enough lime, all the oxide will be converted into carbonate before this stage is reached. On the other hand, if the pressure of the CO_2 is not high enough at the start, none will be absorbed. The important point to notice is that, for a given temperature, the pressure of CO_2 at which the action stops is the same, whether we start with lime and carbon dioxide or with calcium carbonate and no carbon dioxide. A necessary condition, however, is that the quantities present are such that no one of the substances is completely used up before the equilibrium point is reached. This is a good example of a **balanced action**. The action of heat on calcium carbonate may be written



The reversed arrows in such a case express the fact that the action can go in either direction.

418. To sum up, there are reversible actions which can go in either direction and which

(a) can go completely in one direction or the other by removing one of the products of the reaction as it is formed, or

(b) result in balanced actions if all the substances involved are kept together.

419. The action of heat on calcium carbonate in a closed space is thus to split it up into two substances which recombine on cooling. Such an action is called **dissociation**.

A large number of such actions are known, and in many of the most interesting cases the substances produced are all gaseous. Here is an example:

420. If a little ammonium chloride—a white solid—is heated it sublimes, i.e. it passes directly into a vapour without melting. The formula of this salt is NH_4Cl . When it is vaporised we should expect to be able to calculate from this formula the density of the vapour, the temperature and pressure being known by observation. Or, put slightly differently, if a known weight of the substance be heated so as to fill a space whose volume can be measured, we should expect to be able to calculate the pressure obtained. As a matter of fact, when tested by direct experiment, the actual pressure of vaporised ammonium chloride is found to be *more* than the calculated value, and this excess is more marked as the temperature increases, until ultimately the pressure goes up to *twice* the theoretical value. It does not go beyond this. Looking at it from the point of view of Avogadro's Law, this increased pressure suggests that at the higher temperatures we are dealing with *more molecules than have been allowed for*, apparently twice as many. This could easily be explained by supposing that the molecule on heating breaks up into two. In fact, there is little difficulty in accepting this explanation. Ammonia is lighter and so is more diffusible than hydrochloric acid gas, and can be separated from the vapour by

this property. If a dry, porous pot be placed in the vapour, the ammonia diffuses into the pot more readily than the hydrochloric acid. If, then, after immersion for a short time in the vapour a little water be poured into the porous pot, it will be found to be alkaline to litmus, while the ammonium chloride outside has become acid, since the removal of the ammonia has left some free hydrochloric acid (compare with § 268).

The obvious explanation, then, is that an action takes place on heating, represented by the equation



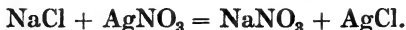
On cooling, the ammonium chloride at once re-forms. This is another case of dissociation. It will readily be seen from the equation that in the case of ammonium chloride, if the volume is kept unchanged, the pressure, when all the chloride is dissociated, will be twice that calculated from the formula. At constant pressure the volume will be double and the density will be half that calculated from the formula.

421. If we were dealing with a substance each molecule of which split into three molecules on heating, the last paragraph would be varied by saying that the maximum pressure would be three times the calculated value, or the minimum density one-third the calculated value.

It must be clearly noted that these are *maximum and minimum* values. The dissociation is not always complete. For example, in the case of ammonium chloride, the density will never be *less* than half the calculated value. It will at first be *more than half*, and as the temperature rises it *decreases to half* as the dissociation approaches completion.

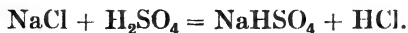
422. Other substances which exhibit dissociation are phosphorus pentachloride ($\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$), and stannous chloride ($\text{Sn}_2\text{Cl}_4 \rightleftharpoons 2\text{SnCl}_2$) and many others. Cases which the reader has already met with and to which he can refer back are represented by the equations $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ and $\text{I}_2 \rightleftharpoons 2\text{I}$.

423. In § 145 (*d*) occurred the statement: "If a precipitate can be formed, it will be formed". The reason for this should now be clearer. Take, for instance, an example which will at this stage be familiar:



If all the four salts concerned were soluble and there were any tendency to exchange partners, it might be expected that a balance-point would be reached, with a definite proportion of all four salts present. But one of them, AgCl, is insoluble and drops out of the solution. The effect of this is much the same as removing hydrogen as it is formed in the experiment with the steam and the red-hot iron. The removal of the silver chloride from the solution severely handicaps the reverse action. Hence the action goes all one way. The astonishing thing about this is that it is the water which really decides what is to happen. Presumably if the experiment were done in a solvent in which silver nitrate was insoluble and the other three salts soluble, then the action would go in exactly the opposite direction, provided there were any tendency for the action to take place at all. What determines this tendency will be a little clearer after reading § 459.

424. Here is another very striking example resembling the last in some points but differing in others. When sulphuric acid is heated with a chloride, hydrochloric acid, HCl, is evolved (see § 393). Naturally this suggests that the sulphuric acid is a stronger acid than hydrochloric acid and so succeeds in turning it out of its compounds. But look at the equation



Of the four substances involved HCl is a gas. Suppose there is some tendency for the action represented by the equation to begin. Say, for example, that the sulphuric acid combines with 1 per cent. of the sodium in the sodium chloride present, forming HCl, and that at this stage the reverse action is sufficiently

active to produce equilibrium. If, now, the mixture is heated, the HCl at once comes off, being a gas, and owing to its removal the reverse action is stopped altogether, and the forward action has it all its own way. In other words the main factor in settling which way the action goes depends upon the apparently trivial fact that HCl is a gas and sulphuric acid a not very volatile liquid. Similarly silicic acid (of which sand or silica, SiO_2 , may be regarded as the anhydride, see § 405) is reckoned a very feeble acid, yet at high temperatures sand in the presence of steam will displace HCl from common salt to form sodium silicate.

Chapter XXVIII

FREEZING-POINT AND BOILING-POINT: IONIC DISSOCIATION

425. We have learned to think of a gas as a number of separate molecules in an otherwise empty space, moving about to all parts of the space and providing by their motion a pressure on the sides of the containing vessel. Avogadro's Law states that equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules, or, put slightly differently, if the same number of molecules of different gases be placed in equal volumes and are at the same temperature they will exert the same pressure. Put this way, the law may seem surprising. A gas exerts a pressure. If then we imagine the gas replaced, molecule by molecule, by a heavier gas, surely the pressure will be greater. After all, the pressure is just the bombardment of the walls by the molecules and heavier molecules must surely produce a greater bombardment. The reader is invited to stop and consider this paradox, and to see if he can recollect the explanation for himself before he reads on. If he cannot, he should re-read the last paragraph in chap. xx. This will clear up the difficulty.

426. To find the molecular weight of a gas we have seen, in chap. vi, that the simplest way is to find out by actual weighing:

- (a) the weight of a number of molecules of the gas, and
- (b) the weight of the *same* number of molecules of hydrogen.

The result of (a) is divided by the result of (b), and this quotient gives the weight of a molecule of a gas compared with the weight of a molecule of hydrogen. The weight of the latter is, for reasons explained in chap. vi, taken as 2 and the mole-

cular weight is easily determined. It is twice the value of the quotient (result of (a)) \div (result of (b)).

The essential point at the back of all this is provided by Avogadro's Law. We never have to consider exactly *how many* molecules there are. What does matter is that there should be the same number in each case. This, says Avogadro, is secured by taking the same *volume* at the same *temperature* and the same *pressure*.

427. The point to be emphasised for our immediate purpose is that temperature and volume being fixed, the pressure is settled by the number of molecules present and *does not depend upon what kind of molecules they are*. This is an interesting aspect of Avogadro's Law. We shall return to it a little later on.

428. A substance in solution in one way at least resembles a gas. A gas always tends to *fill the space* in which it is placed. A substance in solution always tends to *fill the solvent* in which it is placed. There is, however, an important difference. The gas fills its space practically at once; the substance in solution does it gradually. If, however, we consider the mental pictures we must make of the two cases, we think in each case of small particles moving about, "elbowing" and jostling one another. In the case of a gas there is no difficulty in the particles spreading throughout a space. But in the case of a substance in solution the particles have to plough their way through the liquid mass, i.e. between the liquid particles. Without making any definite statement as to exactly what happens, we can see that this might account for the very considerable difference in speed between the two cases.

429. In the case of a gas we were successful in finding a measurable quantity—the pressure—which (temperature and volume being fixed) was determined by the *number* of molecules present and not by what kind of molecules they were, and we were reminded, a paragraph or two back, that this provides a convenient way of finding a molecular weight. We will now consider solutions and see if we cannot find some test by which we can say that two *solutions* contain the same number of molecules.

It will be very convenient if we *can* decide that there *are* the same number of molecules in each of two solutions. It will enable us to compare molecular weights, and with greater ease than in the case of gases, as gases are very light and are not easy to handle so that accurate weighing is a matter of some difficulty, whereas there is no difficulty in determining how much of a solid is **present** in a given solution. It can, for example, be weighed in its ordinary solid state before it is dissolved.

430. Comparing a solution with a gas, the first point that may suggest itself is this. In the case of a gas the movement of the molecules produces a measurable pressure. Can we find any similar pressure due to the movements of the molecules of a substance in solution? Well, we can. It is called the **Osmotic pressure**. Osmotic pressure is a very interesting and important subject. Both the experiment and theory are, however, somewhat beyond our present scope, and for the moment we will just assure the reader that such a pressure does exist and can be measured. We will mention one or two facts about osmotic pressure and then pass on.

Van't Hoff, a Dutch chemist (1852-1911), is mainly responsible for establishing the laws of solution and he arrived at the following very remarkable result:

431. "A substance in dilute solution obeys the gas laws." In considering this statement *osmotic pressure* must be understood instead of the *usual gas pressure* and then the parallel between a gas and a substance in solution is complete. We thus see that the osmotic pressure of a fixed quantity of a substance in solution is directly proportional to the absolute temperature and inversely to the volume. The practical point therefore is that the osmotic pressure is directly proportional to the concentration of the solution. The more gas we introduce into a closed space the more the gas pressure rises. Similarly the more of a substance we dissolve in a definite quantity of a solvent the more the osmotic pressure rises.

432. We may consider a substance in solution as a gas occupying the volume of the solution provided we replace the usual gas pressure by the osmotic pressure.

Corresponding to Avogadro's Law we have: **Equal volumes of solutions of different substances at the same temperature and osmotic pressure contain the same number of molecules.** And, perhaps most striking of all: **The molecular weight in grammes of any substance when dissolved in 22.4 litres of solvent at 0° C. exerts an osmotic pressure of 760 mm. of mercury.**

433. Determinations of molecular weights by measurement of osmotic pressure are not often made, as accurate measurement of the pressures is very difficult. There are, however, two other properties of solutions which also depend upon the number of molecules present and not upon their kind. These yield methods of finding molecular weights which are in many ways simpler than the use of osmotic pressure. To these we will now turn. They hinge upon **the effect on the freezing-point or the boiling-point of a liquid produced by dissolving a substance in it.**

It has long been known that **the presence of a solid in solution in a liquid lowers the freezing-point.** Sea water, for example, freezes at a lower temperature than fresh water. *The amount of this depression, like the osmotic pressure, depends upon the number of molecules present per litre and not upon their nature.* We can test this quite simply by trying the effect of dissolving the same numbers of molecules of different substances in the same amount of water. Since the gramme-molecule of different substances always contains the same number of molecules, we can easily arrange that the numbers of molecules shall be the same by choosing several compounds and taking the gramme-molecule of each, or the same fraction of it, and the same volume of water. Thus the molecular weight of urea is 60 and of quinol, $\text{C}_6\text{H}_4(\text{OH})_2$, 110. If, then, we take two equal quantities of water and dissolve in one 60 gm. of urea and in the other 110 gm. of

quinol, we know that we have dissolved the same number of molecules in each case. If these two solutions are cooled by a freezing mixture and the temperatures at which freezing begins are taken by a sensitive thermometer, *they are found to be the same for both solutions.*

434. In particular, the molecular weight in grammes of a substance dissolved in a litre of water lowers the freezing-point by 1.85°C . To this rule there are some *apparent* exceptions. These apparent exceptions are important, particularly as they consist of those compounds which are decomposed by an electric current. This matter will be discussed more fully later.

It must be noticed that the amount of the depression is not the same for all *solvents*. We shall, however, only consider water for the present.

435. The actual depression of the freezing-point for weak solutions is directly proportional to the strength of the solution. Note here that the solutions must be *dilute* and also that the solid which separates out on freezing must consist of the *solvent only*. This is called **Blagden's Law** and may be tested easily enough by direct experiment. It will thus be seen that the lowering of the freezing-point for a solution of known strength supplies a method of finding the molecular weight of the solute. The following example will make this clear:

It is found that 8.5 gm. of pyrogallol dissolved in 250 c.c. of water depress the freezing-point by 0.5° . What is the molecular weight of pyrogallol?

A solution of 8.5 gm. in 250 c.c. would contain 34 gm. in 1000 c.c. Since the actual depression of the freezing-point is proportional to the strength of the solution and 34 gm. in 1000 c.c. depress the freezing-point by 0.5° , the amount which dissolved in 1000 c.c. would depress it by 1.85° is clearly $\frac{34 \times 1.85}{0.5}$, which is 126 gm.

Hence 126 gm. of pyrogallol dissolved in a litre of water

depress the freezing-point by 1.85. So 126 must be the gramme-molecular weight and hence 126 is the value of the molecular weight of pyrogallol given by the experiment.

Thus the question: "What is the molecular weight of this substance?" may be re-worded "How many grammes of this substance must be dissolved in 1000 c.c. of water in order to lower the freezing-point $1.85^{\circ}\text{C}.$?" Remembering Blagden's Law, this is just a question of simple "rule of three."

436. It is also found that the **presence of a substance in solution raises the boiling-point.** The rules governing this rise are exactly like those governing the depression of the freezing-point. A gramme-molecule of a substance dissolved in a litre of water raises the boiling-point by $0.52^{\circ}\text{C}.$ Boiling-points are more difficult to work with accurately than freezing-points. For really successful work the temperatures must be correct to something like a hundredth of a degree, and in practice accuracy of this sort is more easily attained in observing the freezing-point than in observing the boiling-point. So as the freezing-point method is a very good one the boiling-point method is less used.

437. The reader will probably by now be somewhat mystified about one point. We have mentioned urea, sugar and quinol and pyrogallol, substances of which we had previously heard little or nothing. Why were they selected? Why not the familiar substances—common salt, caustic potash, copper sulphate? Well, for a very good reason. These substances would have given us such apparently irregular results that the laws we have just been discussing would have been quite masked. It takes a good deal of further discussion and explanation before these discrepancies can be cleared up. By the organic substances mentioned the laws are for the most part clearly and obviously obeyed. For solutions of acids, alkalis and salts the observed changes are all larger than these laws require, frequently very much larger. The osmotic pressure, the depression of the freezing-point and the raising of the boiling-point are all greater than we should expect

from the known molecular weights and the theory of solutions so far as we have discussed them. How much greater? That all depends. Two rules may be stated at once which can be directly checked by experiment:

438. (1) The osmotic pressure, the depression of the freezing-point and the raising of the boiling-point are for acids, bases and salts all greater than the laws of solutions would lead us to expect, and this departure from the laws gets more and more pronounced as the solutions observed are more dilute.

439. (2) The osmotic pressure, the depression of the freezing-point and the raising of the boiling-point in such cases tend, as the solution gets weaker, each to a value twice the theoretical value or three times the theoretical value. More rarely it may be four times or perhaps even more, but in any case it will be a small whole multiple.

440. According to tables prepared by the American chemists, Noyes and Folk (1910), for solutions containing one-tenth of the gramme-molecule per litre, the following are the values to three places of decimals for the depression of the freezing-point in two actual cases:

NaCl 0.348°C. , CaCl_2 0.489°C.

If these substances had obeyed the rules as they have been given for urea, etc., the values would have been 0.185°C. in each case. It will be noticed that for NaCl the value is nearly *twice* the expected value and that for CaCl_2 it is *more than twice and less than three times* the expected value. If these depressions are measured for still more dilute solutions, the difference between the expected values and the actual values becomes more marked. For very dilute solutions this actual value for NaCl is twice the expected value, but however dilute the solution it is *never more than twice*. For very dilute solutions of CaCl_2 the actual value is three times the expected value, but however dilute the solution it is *never more than three times*. The osmotic pressure shows the same variation from the expected values.

441. All through the discussion of solutions we have been comparing a substance in solution with a gas. We may reasonably ask, Is the pressure of a gas ever more than we should expect from the formula of the molecule? And if such cases are known, Is the value observed twice (or other small whole multiple of) the value we should expect from the formula?

It has already been mentioned (§ 187) that the vapour of iodine at lower temperatures corresponds to the formula I_2 , but at higher temperatures it is monatomic. If we first of all established that the molecule of iodine was I_2 , and then assumed this represented the molecule at very high temperatures, we should find that the pressure was just twice as great as we expected. The doubling of the pressure is at once explained if we assume that the molecule is then represented by I and not by I_2 .

442. Again, a reference back to § 420 will recall a very similar difficulty in the case of the pressure of the vapour of ammonium chloride. There the value was too large for the formula, but never more than twice the expected value. The case of ammonium chloride is one of several which have been referred to, all explainable in the same way, i.e. by supposing that at higher temperatures the molecules split up or dissociate into simpler ones. Hence, there are more molecules present than have been allowed for, and so the pressure appears to be too big.

443. Now consider a solution of common salt. The osmotic pressure and the depression of the freezing-point are greater than they would be if the solution contained just molecules of $NaCl$, and for very dilute solutions the values are twice the expected values. Hence we appear to have more molecules present than we thought. The suggestion that each molecule has split up into simpler molecules is a very obvious one. It is a line of explanation similar to that which proved so helpful in the case of dissociation in gases. The fact that the difference between the expected values and the real values gets more marked as the solution gets weaker (i.e. as the molecules of $NaCl$ occupy a larger

space) corresponds to the increase of the dissociation of ammonium chloride on heating. Heating promotes expansion, and so the molecules tend to occupy a larger space. The heating in the one case and the dilution in the other have this in common, namely that they both tend to separate the molecules—to demand for them in fact “more elbow room”. The fact that in both cases the pressure tends to a maximum value double the expected value is also most striking. But how can sodium chloride split up to give twice the number of molecules? There is only one possible way for a molecule of the salt to split up and that is *into an atom of sodium and an atom of chlorine*. The reader may be pardoned if he finds it difficult to believe that this is actually what does happen. In their familiar forms, sodium is an active, light silvery metal which acts violently upon water; chlorine is a greenish gas with a pungent smell. How can these two exist separately in the solution? Yet we are driven to conclude that they do. This is further borne out by the fact that a substance like calcium chloride, CaCl_2 , gives for dilute solutions a value for osmotic pressure, depression of the freezing-point, etc., three times the normal value, suggesting it splits up into *three* parts, Ca, Cl and Cl.

444. We must suppose, however, that substances in this dissociated state are, in some way we cannot pretend exactly to understand, in a physical condition differing widely from their condition as ordinary molecules of the free substances. There is then some evidence for this splitting up. The reader will perhaps be more and more convinced of it as he pursues the subject.

The view put forward is, then, that many acids, alkalis and salts in dilute solution split up into what are in many ways separate parts or **ions**. Of these ions, more will be heard in the next chapter. The ions behave for the most part like separate molecules.

Chapter XXIX

ELECTROLYSIS: IONIC DISSOCIATION (contd.)

445. When the wires from the two terminals of an electric battery or from the electric main are placed in a liquid and kept apart, one of three things may occur. They are:

- (a) No current passes.
- (b) The liquid carries the current like any other conductor.
- (c) The liquid carries the current and is decomposed in the process, different products of the decomposition appearing at the anode and at the kathode. By "anode" is meant the end of the wire where (according to the accepted convention) the current enters the solution, the end where the current leaves the solution being the kathode. The kathode may also be considered as the terminal where negative electricity is entering the solution. This will be clear to the reader who has studied electricity. The reader who has not had better accept what he is told here for the present, resolving to look further into the matter as soon as he has the chance. The less a student of science takes for granted just because he is told it, the better.

Considering the three cases mentioned above, case (a) merely means that the liquid is a non-conductor, like, for example, *pure* water or paraffin oil. (b), of which mercury provides an example, also calls for no comment. It is (c) which interests us now. Before reading further the student should recollect the cases of electrolysis with which by now he should be familiar, viz., water (§ 50), HCl (§ 195), NaCl (§ 176).

Liquids which are decomposed by a current are called **electrolytes** and—notice this particularly—they are the *same substances which* we have been forced to admit—reluctantly perhaps—*split up into ions in dilute solution*. But on second

thoughts this is not surprising. If the substance is already decomposed, it is all the easier for the current to separate the products of the decomposition. In other words, if we accept the ionic view, electrolysis does not consist in a *splitting up* but in a *sorting out*. The mere act of solution has done the splitting up. But how has this sorting occurred? To explain this we must levy another tax upon the imagination. A full and adequate explanation is beyond our scope here. What follows is given to help the reader to form a mental picture of what is going on. He must be prepared to see it modified when he makes a more advanced study of the subject.

Our explanation, then, is this. We have seen that we may think of the anode or positive pole as a place where positive electricity is being introduced into the solution. Now it is a simple electrical fact that positively charged bodies attract negatively charged ones. If then we suppose that those ions which appear at the anode carry a negative charge of electricity, it is easy to see why they get there. They are in the solution and carry a negative charge. It is just a case of electrical attraction which causes them to appear at the anode. Similarly, if the other ions carry a positive charge they will appear at the kathode.

446. This is worth considering a little more closely. Suppose an electric current be made to pass in series through several electrolytes—say silver nitrate solution, dilute hydriodic acid, dilute hydrochloric acid, dilute sulphuric acid and copper sulphate. At the kathode, silver is released in the first case, hydrogen in the next three and copper in the last. We find by actual trial that in each case when hydrogen is liberated we get **the same amount of hydrogen**, and that in the cases of hydrogen and both the metals the amounts liberated are **proportional to their chemical equivalents**. This is a very striking result. If, for example, the experiment is continued until 1 gm. of hydrogen is given off from the sulphuric acid, a gramme of

hydrogen will be given off from each of the other acids, and at the same time 108 gm. of silver and $\frac{63}{2}$ gm. of copper will be deposited from the other two solutions respectively.

447. The laws of electrolysis were first worked out and published by Michael Faraday (1791–1867) as far back as 1832, about fifty-five years before the above theory was developed. Before we state them it may be emphasised that the laws are fundamental and must be studied with the greatest care. They are the result of direct experiment and form the basis of the whole theory of electrolysis. Faraday's laws were stated in a form which does not exactly fit in with modern ideas. Put into modern scientific language they may be stated thus:

448. Faraday's First Law. The amount of any ion liberated by the passage of an electric current is proportional to the amount of electricity passed, or in other words, it is proportional to the current and to the time for which that current is passed.

Faraday's Second Law. If an electric current is passed through a series of electrolytes, the weights of the different ions liberated are proportional to the chemical equivalents of those ions.

449. The student, whether he has studied electricity or not, probably knows the name "ampere" as the ordinary unit of current. As a particular example of Faraday's First Law, an ampere deposits silver from a silver salt at the rate of 0.001118 gm. per second. The ampere was originally fixed for reasons which suited physicists. They have found, however, that Faraday's Law is such a useful one in practice that the ampere is now *defined* as the current which deposits 0.001118 gm. of silver per second from a solution of silver nitrate. and any current can be measured by seeing how fast it deposits silver. The amount of any ion released by a current of 1 ampere in 1 second is called the **electro-chemical equivalent** of that ion.

450. It can be immediately deduced from Faraday's Second Law that:

The electro-chemical equivalents of different ions are proportional to their chemical equivalents.

To see this, apply the second law to the case where the current is 1 ampere and the time 1 second. The "weights of the different ions liberated" are then the electro-chemical equivalents, which are thus, by the law, proportional to the chemical equivalents. To see the usefulness of this, suppose the electro-chemical equivalent of copper is to be calculated. Let it be x . The chemical equivalent of silver is 108 and of copper it is $\frac{63}{2}$, or 31.5. Hence by Faraday's Second Law

$$\frac{108}{31.5} = \frac{0.001118}{x},$$

from which x is easily found to be 0.000326. By examining this example it can be seen that the electro-chemical equivalent can at once be found from the chemical equivalent by multiplying the latter by the factor $\frac{0.001118}{108}$. The reader will also easily see how to find the chemical equivalent from the other.

451. If the student will turn to the chapter in his algebra book on variation and proportion, he will have no difficulty in expressing Faraday's Laws in one simple formula. If W be the weight of an ion released by C amperes in t seconds and ϵ be its chemical equivalent, then Faraday's Laws may be expressed in symbols

$$W \propto C\epsilon t \quad \text{or} \quad W = kC\epsilon t.$$

where k is the same for any experiment, any ion, any current and any time. So if it can be found for any special case it is known once and for all. Taking the case of silver, the formula becomes

$$0.001118 = k \times 1 \times 1 \times 108,$$

or
$$k = \frac{0.001118}{108},$$

a value which k always has if C be in amperes, t in seconds and W in grammes.

$$\text{Hence} \quad W = \frac{0.001118}{108} \times Ct\epsilon.$$

The product $k\epsilon$ is clearly the electro-chemical equivalent. It is, however, much better to worry every case out from the laws than blindly to apply the formula.

452. The electro-chemical equivalent of copper can be obtained practically by the following experiment:

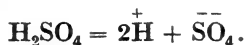
A current—say from an accumulator—is passed in series through a voltmeter containing dilute sulphuric acid, through a solution of copper sulphate and through an ammeter, the latter being an instrument for measuring current in amperes. The hydrogen liberated at the kathode from the sulphuric acid is measured, and after suitable correction for temperature, pressure and moisture, its weight is calculated. The kathode in the solution of copper sulphate consists of a copper plate, carefully cleaned, dried and weighed. The current is allowed to run for some time, which is observed to the nearest second, the amperes being read at frequent and regular intervals as the current may vary a good deal. The average current is calculated and the electro-chemical equivalent of copper is found by simple proportion. The question becomes: if so many amperes* in so many seconds deposit so much copper, how much copper will 1 ampere deposit in 1 second? Or, of course, the formula may be used. And so also for the hydrogen. The experiment can clearly be extended to other ions.

453. To understand more clearly what happens, it is necessary to try and get some picture of the process in the mind's eye. Consider a simple case. Suppose there is an ionised solution

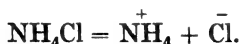
* The reader who is studying physics will see that, by using a tangent galvanometer, this experiment will give the galvanometer constant (the "reduction factor") by assuming the electro-chemical equivalent and calculating the amperes.

of hydrochloric acid, i.e. a solution containing chlorine ions with negative charges and hydrogen ions with positive charges. One is apt to think of positive and negative electricity as things which together completely "cancel out" like a debit and a credit or as the waves and troughs on a rough piece of water cancel out when the storm subsides. But accepting the conclusions of the physicists, positive and negative electricity are quite different things and their mutual action is more like that of buttons and button-holes or nuts and bolts—the one the counterpart of the other. So the solution of hydrochloric acid contains two distinct kinds of ions, differing both in their chemical nature and in the nature of their electrical charges. Suppose also there is a similar solution of silver nitrate and that a current is passed both through the hydrochloric acid and the silver nitrate. Now look at it like this. If an electric current flows round a single closed circuit, the current is the same at every point in that circuit. Hence the same amount of electricity goes through each of the electrolytes. There is as much negative electricity passing into the hydrochloric acid as into the silver nitrate. For every gramme of hydrogen liberated in the former, 108 gm. of silver are liberated in the latter. Now 108 is the atomic weight of silver. Therefore for every *atom* liberated in the one case one *atom* is liberated in the other. Now dismiss the question of silver and hydrogen. Think of it only as a question of electrical attraction. Clearly viewed as an electrical action it is reasonable to suppose that the action is the same in each electrolyte. So much electricity is passed in; the same amount of electricity of opposite sign is neutralised on the ions and the ions then cease to be ions and are liberated. Hence it follows that the silver and the hydrogen ions—or any other univalent ions—carry each the same charge of electricity. It will also be clear that the copper ion carries twice this charge, for the amount of electricity which releases two ions of silver or hydrogen only releases one of copper. We have then something

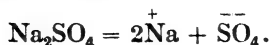
like an "atomic" theory of electricity. There is a small natural unit of electricity, carried by any univalent ion. Any bivalent ion carries twice that quantity, any trivalent ion three times the quantity and so on. Metals and hydrogen carry positive charges; ions consisting of acids without their hydrogen and also the OH ions of alkalis carry negative charges. This can be indicated by writing plus and minus signs over the symbols, one + sign indicating the quantity of electricity carried by a univalent positive ion, and one - sign indicating the quantity of electricity carried by a univalent negative ion. Thus, an ion of sodium is written $\overset{+}{\text{Na}}$ and of chlorine $\bar{\text{Cl}}$; of copper $\overset{++}{\text{Cu}}$ and so on. An ion may be of an element or of a compound radical. Thus the "ionisation" of sulphuric acid when water is added may be written



$\bar{\bar{\text{SO}}}_4$ is sometimes called "sulphion". Similarly, the change in ammonium chloride on solution is shown in an equation thus:



454. An element or radical liberated by electrolysis frequently reacts with water or with the metal of the wire carrying the current, and the result is that it is not the ion which actually appears, but the product of this further action. Thus in the case of sulphuric acid the "sulphion" acts with the water, combining with the hydrogen and releasing oxygen. Quite a number of salts give oxygen and hydrogen on electrolysis. For example, sodium sulphate ionises thus:



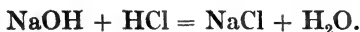
The sodium which is liberated by electrolysis in the presence of water gives hydrogen and caustic soda, and the SO_4 gives sulphuric acid and oxygen as before. The net result in the solution is that the liquid round the kathode becomes alkaline

and round the anode acid, as may be shown by adding a little litmus. If the liquid be shaken up after the electrolysis, the sodium sulphate is reconstructed unchanged, some water has vanished and the solution has become a little stronger.

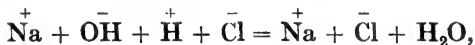
Similarly, potassium hydroxide, KOH, yields ions of $\overset{+}{K}$ and $\bar{O}H$. On electrolysis, the former give hydrogen and reproduce KOH at the kathode, and the OH ions give oxygen and reconstruct water at the anode thus:



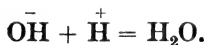
455. Let us now consider what happens when an acid and an alkali are mixed together, for example caustic soda and hydrochloric acid. The equation is



Suppose this written down in its ionised form. It becomes



or, omitting the ions which occur on both sides, and so take no part in the action,



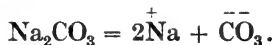
Expressed in words, this means the positive charge on a hydrogen ion and the negative charge on an OH ion neutralise each other and the two ions combine to form a molecule of water. This is a very striking result; the particular acid and alkali used do not appear in this simplified form of the equation. The action is exactly the same whatever acid and alkali are used, provided that both are completely ionised at the start. Whether they are completely ionised or not can be seen from the depression of the freezing-point and the other properties depending on the number of molecules present. There is an additional piece of evidence here in favour of the truth of the ionic theory. Suppose we take enough of two or three different dilute acids to contain the same

amount, say 0.1 gm., of hydrogen each. That would mean 4.9 gm. of sulphuric acid, 3.65 gm. of hydrochloric acid and so on. If, then, these equivalent quantities of the different acids are neutralised with an alkali—any alkali so long as it is completely dissociated—it is found that the same amount of heat is produced in every case. The temperature in each case must be noted before and after mixing. It might be thought that if the same amount of heat is produced in each case, then, provided we use the same volumes of water, the same temperatures would be observed. But this would ignore the fact that it requires a different amount of heat to raise a gramme of different substances 1° C., i.e. there is a difference in "specific heat". To complete the investigation we require to know the weight of each solution, its specific heat and the "water value" of the containing vessel. With the rise of temperature observed, the number of calories generated can then be calculated. If the reader will turn to the chapter on "specific heat" in his text-book of Heat, he will have no difficulty in completing this. The fact to be noted is that, provided the solutions are so dilute that the dissociation is practically complete, the amount of heat produced is the same in each case. This is a very striking confirmation of the ionic theory.

456. The idea of ions has now led us to new conceptions of acids and alkalis. Once the ionic view is accepted we can regard an acid as a solution which contains hydrogen ions and an alkali as one which contains "hydroxyl" or OH ions. The idea of an acid thus passes through three stages as we progress. First there is the crude "finger-print" idea, that an acid is something which turns blue litmus red (§ 35). This is followed by the more developed view of an acid as containing hydrogen replaceable by a metal to form a salt, the view on which the definition of an acid (§ 147) was based. Now we have this third stage, depending upon the presence of hydrogen ions. For the idea of an alkali there are, of course, three similar stages.

457. Consider another fact. *Dilute* solutions of sodium chloride and potassium nitrate are mixed. The mixture contains the four ions Na^+ , K^+ , Cl^- , NO_3^- . Now suppose the original salts had been potassium chloride and sodium nitrate. If the ionic hypothesis is true the solution contains the same four ions, and provided the quantities are the same, there should be no difference whatever between the two mixtures. This is in fact found to be the case, and moreover there is not the slightest change in temperature upon mixing. This is worth thinking about. A belief in these ions is not arrived at by one bit of evidence. The facts as they come into view strengthen the belief into a conviction.

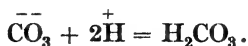
458. Here is another set of facts which the theory explains simply and well. Some salts which look at first glance as if they should be quite neutral turn out to be alkaline. Sodium carbonate is a good example of this. The splitting up of this salt into ions presumably takes place thus:



But the solution is alkaline, and so would be expected to contain OH^- ions. Carbonic acid, H_2CO_3 , is a very feeble acid which is scarcely ionised at all. A reasonable explanation of what takes place is this. Water ionises slightly thus:



Carbonic acid being a *very* weak acid tends to form undissociated molecules as far as possible thus:



This removes H^+ ions and, since the dissociation of water is a reversible action, more water dissociates into H^+ ions and OH^- ions. The CO_3^{--} ions continually remove the H^+ ions to form more molecules of H_2CO_3 , leaving OH^- ions in solution. These OH^- ions

cause the alkalinity. It should be noticed that this explanation only requires us to assume that the water is *slightly* ionised to explain *considerable* alkalinity in the solution of sodium carbonate.

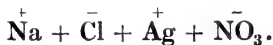
Borates of sodium and potassium are similarly alkaline and so are the sodium and potassium salts of many weak organic acids, e.g. soap (see § 233). Similarly some salts are acid. Aluminium sulphate is a good example of this. In this case it is the hydroxide of aluminium which is scarcely ionised. So the aluminium ions tend to form undissociated molecules, $\text{Al}(\text{OH})_3$, with the OH^- ions formed from the water, leaving H^+ ions, and the presence of these hydrogen ions is shown by the solution being acid to litmus.

Note that the total positive and negative charges in a solution exactly balance. The solution as a whole is not electrified.

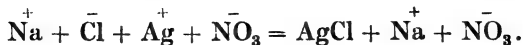
459. The ionic theory also carries a stage further the explanation of the formation of a precipitate by double decomposition. The rule (see §§ 145 (*d*) and 423) is that if a precipitate can be formed it will be formed, and in the explanation in § 423 it was assumed that there was a tendency for the precipitate to begin to form. This tendency is clearly to be expected if the salts used are ionised. Revert, for example, to the equation



The left-hand side may in dilute solution be written



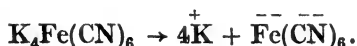
We now see that the action is not between sodium chloride and silver nitrate, but between silver ions and chloride ions, which unite to form molecules of insoluble silver chloride. The equation is



These molecules of silver chloride being insoluble drop out of

the solutions. There is then no tendency for the molecules so formed to dissociate again. There is thus a steady loss of Cl and Ag ions which goes on until there are no more of one or other in the solution.

460. Note, too, that *in such salts as potassium ferricyanide* ($\text{K}_3\text{Fe}(\text{CN})_6$) *and potassium ferrocyanide* ($\text{K}_4\text{Fe}(\text{CN})_6$) *the iron does not form positive ferric or ferrous ions of the usual type, but forms complex negative ions with the* $(\text{CN})_6$. Potassium ferrocyanide, for example, ionises thus:



These salts do not give the ordinary reactions for ferrous or ferric salts. This is easily explained if we agree that they do not contain the usual ferrous or ferric ions.

461. It is worth noting that the ionic theory explains one useful and common fact of great importance in identifying substances. This is best seen by an example. If dilute sulphuric acid is added to a solution of a barium salt, there is produced a heavy white precipitate of barium sulphate— BaSO_4 . This is used as a common test for barium in solution. It is so usual to come across statements like this that one is apt not to be surprised at the fact that the test works with practically any barium salt. But it would not have been extraordinary if there had been no general test for *all* soluble barium salts. There is no such handy test, for example, for all substances containing, say, phosphorus. The ionic theory explains this. All solutions of barium salts contain barium ions and all these ions are identical. Hence it is easy to see why the same test serves in every case. Compare this with the case of iron. All ions of iron are not identical. There are “ferrous” (Fe^{++}) and “ferric” (Fe^{+++}) ions and the tests for the two kinds are quite different. Such tests, moreover, are not applicable to salts like the ferrocyanides, referred to in § 460.

462. The ionic theory gives, so far as ions are concerned, a more obvious meaning to valency. The valency in such a case is seen to be the number of "atoms of electricity" an ion carries, the "atom of electricity" being the charge carried by a hydrogen ion. Such elements as iron, tin, etc., which in different compounds can have two valencies have, of course, also two chemical and two electro-chemical equivalents.

Chapter XXX

OXIDATION AND REDUCTION; SOME COMMON OXIDISING AGENTS

463. In chap. iv the process of combining with oxygen was called "oxidation" or "oxidising", and in chap. v the reverse process, the removal of oxygen from a compound, was termed "reduction". The reader was also told that these terms were used also in a somewhat wider sense and that this would be explained later. Before we proceed to keep that promise, let us consider the subject a little more closely in the light of what we already know.

Substances which can be used to oxidise other substances are called oxidising agents and are of two kinds:

(1) Substances with plenty of oxygen with which they readily part. Such are nitric acid and nitrates; chlorates; peroxides such as sodium peroxide, lead peroxide, barium peroxide, manganese dioxide; dichromates and permanganates.

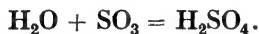
(2) Substances which oxidise others indirectly in the presence of water. These substances have a chemical attraction or "affinity" for hydrogen and as the substance to be oxidised has an attraction for oxygen, the two between them split up the water. The oxidising agent gets the hydrogen, and the oxygen thus freed performs the oxidation.

464. The commonest and most important example of the latter type is chlorine whose bleaching powers, explained in chap. xvii, are an example of its working as an oxidising agent. Bromine, we have seen, acts similarly but less strongly. There are a number of "per" salts which act in a somewhat similar way. These salts contain a larger share of the negative radical in the molecule than the ordinary salts. Compare, for instance,

potassium sulphate, K_2SO_4 , with potassium persulphate, $K_2S_2O_8$. Acid solutions of the latter will yield oxygen when they are warmed. If the acid solution is brought into contact with an oxidisable substance, this substance is oxidised and the oxygen is not evolved.

There are a number of tooth pastes and tooth powders on the market which profess to cleanse the teeth by liberating oxygen in the mouth. Some of these contain "per" salts and the like. Others contain peroxides.

465. Before proceeding further, a slight digression may be helpful. Some acids—e.g. sulphuric acid—can be obtained directly from the non-metallic oxide, the "anhydride", and water. In the case of sulphuric acid the anhydride is SO_3 and the acid formed according to the equation



To remind us of this origin of sulphuric acid we could write its formula $H_2O.SO_3$. This is a reminder only. It has one big disadvantage. It suggests that one of the four oxygen molecules is combined in the molecule differently from the other three, whereas in actual fact the acid yields in solution an ion $\bar{S}\bar{O}_4$ in which there is no evidence at all that one oxygen atom is to be distinguished from the others. Similarly, since a salt is formed by replacement of the hydrogen by a metal, such a salt as copper sulphate could be written $CuO.SO_3$. Again we must remember that the four oxygen atoms are all alike. It has been mentioned before that little is known about the structure of molecules in the solid state, but in dilute solution the four oxygen atoms appear to be similarly arranged in the molecule.

Some salts, however, on heating do split into the anhydride and the oxide of the metal. A very familiar case of this is calcium carbonate:



When it suits us to remind ourselves of this connection between

the oxide of the metal and the anhydride of the acid, we shall sometimes write a salt of an acid containing oxygen as the compound of two oxides. This is to help us follow its reactions and chemical relationships and is not meant to be a better picture of how the salt is actually constituted.

466. Ferrous oxide, FeO , is the simplest oxide of iron. In it the valency of iron is two. Corresponding to this basic oxide are a number of salts, ferrous sulphate (FeSO_4), ferrous chloride (FeCl_2), etc. Ferrous oxide is very easily oxidised to ferric oxide, Fe_2O_3 , in which the valency of iron is three, and corresponding to it are a number of ferric salts, $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 and so on. We may show the connection between the two sulphates of iron and the two oxides by writing the formulae in the way just described, thus: $\text{FeO} \cdot \text{SO}_3$, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$. Viewed in this way the change from ferrous sulphate to ferric sulphate is not unnaturally considered as an oxidation. Any suitable oxidising agent in the presence of sulphuric acid will easily effect the change. For example, using hydrogen peroxide, the equation is



But an exactly similar action occurs with ferrous chloride and hydrochloric acid thus:



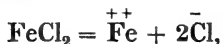
Here neither ferrous chloride nor ferric chloride contains oxygen. Yet the action is still considered as oxidation, and the ferrous chloride is said to be "oxidised" to ferric chloride.

Further, if chlorine is passed into ferrous chloride solution or over heated ferrous chloride, the action is as expressed by the equation



Here again the action is still regarded as oxidation. If the reader will study the above examples in order, he will begin to understand the paradox of calling a process "oxidation" even when there is no oxygen in the action at all.

467. Now look at the same thing from the ionic point of view. What is the difference between the ferrous and ferric ions? There is no perceptible difference between the chlorine ions in dilute solutions of ferrous and ferric chlorides, whereas the positive ions are so different that they might be mistaken for two different metals, were it not that there is no difficulty in turning one into the other. The ionisation which takes place in solution may be represented thus:



Here it is clear at once that the process of oxidation increases the charge on the positive ions. This is an interesting view of oxidations of this kind. The reverse process, reducing the charge, is "reduction". The charge may be entirely removed and in such a case the ion remains an ion no longer, but is reduced to the free metal.

468. After reading this carefully the student should begin to see that there is nothing unreasonable in applying the term reduction to both of the following reactions:

- (1) Conversion of ferric chloride to ferrous chloride.
- (2) Obtaining a pure metal from its oxide by heating it with carbon or hydrogen.

469. It should be recalled here that the addition of hydrogen to an element or compound is regarded as a reduction and the removal of hydrogen as an oxidation. Thus in § 307 the nitric acid was successively *reduced* to lower oxides of oxygen, to nitrogen and finally to ammonia. To convert CO_2 to CO is a reduction, to convert this to carbon is a further reduction, and if the action could by any means be continued further to produce C_2H_2 or CH_4 this would be called a still further reduction.

Just as a substance which readily supplies oxygen is an

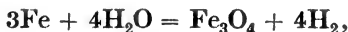
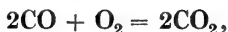
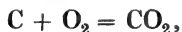
oxidising agent, so anything which readily supplies hydrogen is a reducing agent. Examples of the latter are zinc or tin in the presence of dilute HCl and sodium or potassium in presence of water.

470. It will be recollected that hydrogen (or any other gas) immediately it is liberated by a chemical action is in a specially active state. Such hydrogen is frequently called "nascent hydrogen" (see § 49). It will in many cases effect a reduction which could not be brought about by merely passing in gaseous hydrogen. It must be remembered however that the activity of so-called nascent hydrogen is dependent upon the energy of the reaction which produces it.

471. Stannous or ferrous salts in presence of acid act as reducing agents. Among organic compounds, an important class called "aldehydes" and several different kinds of sugar are reducing agents.

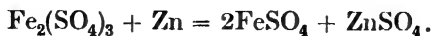
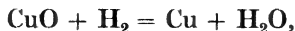
472. The following equations, some of which are fresh to the reader, will illustrate these points.

Oxidations:



(Here the hydrochloric acid is "oxidised to chlorine", this being an example of oxidation which consists of the removal of the hydrogen.)

Reductions:



473. A good example of a reduction is the formation of cuprous oxide from Fehling's solution. This solution contains copper sulphate, caustic soda and a soluble tartrate. On heating the mixture with grape sugar a red precipitate of cuprous oxide, Cu_2O , is formed. Copper sulphate is a cupric salt, derived from the basic oxide CuO . This is a striking reaction and takes place with a number of organic reducing agents, of which grape sugar is one. It is much used practically.

474. It is worth noting that an oxidation and a reduction very frequently go together. When a substance is "oxidised" the oxidising agent is "reduced"; when a substance is "reduced" the reducing agent is "oxidised". To refer back to a familiar case, when hydrogen is passed over red-hot copper oxide, the oxide is reduced and the hydrogen oxidised. How the action is classified depends in most cases on where our interest is fixed. For example, when strong HCl is heated with MnO_2 , if we are considering the acid we say it has been "oxidised", but if our attention is fixed upon the MnO_2 we say it has been "reduced".

475. To sum up, then, we have apparently different types of action which are all classed as oxidations, viz.:

- (1) The addition of oxygen.
- (2) The removal of hydrogen.

(3) The decrease of the relative amount of the metallic or electro-positive constituent of the molecule, or the increase of the positive charge (and so of the valency) of the electro-positive ion in a salt.

The opposite processes are classed together as reductions, namely:

- (1) The removal of oxygen.
- (2) The addition of hydrogen.

(3) The increase of the relative amount of the metallic or electro-positive constituent of the molecule, or the decrease of the

positive charge (and so of the valency) of the electro-positive ion in a salt.

The earlier part of the chapter should be studied carefully to make it clear why processes which do not at first appear similar are here classed together. The reasonableness of this classification will become more and more apparent as the reader studies more and more actual cases of oxidation and reduction in his future work.

476. It will be well at this point to look a little more closely at one or two oxidising agents about which we have so far heard little or nothing.

Hydrogen peroxide, H_2O_2 . One of the most satisfactory of all such substances is hydrogen peroxide, H_2O_2 (see § 684). Its great charm will be obvious. When its work is done the only by-product left is water. It is a very model of tidiness. It leaves no mess to be cleared up after it.

This peroxide has been obtained pure and crystalline at a low temperature. This is of academic interest only. The ordinary hydrogen peroxide of the laboratory or of commerce is a water solution. Such a solution is obtained by adding dilute sulphuric acid to barium peroxide, BaO_2 , and keeping the mixture cool. Certain other peroxides (e.g. Na_2O_2) can be used, but as both the peroxide and sulphate of barium are insoluble, they can be filtered off, leaving the sulphuric acid as the only impurity to be dealt with. By using the correct quantity of barium peroxide the acid can be nearly all used up and a fairly pure water solution of hydrogen peroxide obtained. Barium peroxide has already been met with in connection with the Brin process for making oxygen (see § 38).

477. Hydrogen peroxide is unstable and is easily decomposed by heat or by certain catalytic agents—finely divided metals, manganese dioxide, etc.—into water and oxygen. It can, however, be concentrated up to about 45 per cent. strength by heating, the temperature not being allowed to rise above $70^\circ C$.

Further concentration can be effected, the water being evaporated away by reducing the pressure in a desiccator containing concentrated sulphuric acid. The water passes into vapour and the vapour as it is formed is removed by the sulphuric acid. So there is a steady transference of water from the peroxide solution to the sulphuric acid. In this way the solution may be raised to about 50 per cent. strength.

478. Hydrogen peroxide directly oxidises many substances. It oxidises sulphides and sulphites to sulphates, e.g. it turns lead sulphide, which is black, to lead sulphate, which is white:



Old pictures containing lead paints are often black from the continued action of sulphur in the air. Washing with dilute hydrogen peroxide is a stage in the process of their renovation. It also oxidises, in the presence of dilute acid, ferrous salts to ferric salts, and it liberates iodine from a solution of potassium iodide: $2\text{KI} + \text{H}_2\text{O}_2 = 2\text{KOH} + \text{I}_2$. The iodine liberated will colour starch solution blue (see § 187).

Hydrogen peroxide, like another oxidising agent, chlorine (see § 180), has very marked bleaching properties.

“The lady who dies a chemical yellow
Or stains her grey hair puce”

usually starts the process by removing with peroxide the hue nature allotted to her hair, before replacing it by a tint more to her taste. It can be used for bleaching fabrics too delicate to be treated with chlorine. This particularly applies to substances of animal origin such as wool or silk.

479. A curious type of action in which the peroxide takes part is illustrated by its effect upon silver oxide:



Silver oxide is not very stable, and we have the rather unexpected phenomenon of two loosely held oxygen atoms

combining together and both substances being reduced. Another example of this will occur later. This case justifies the caution exercised in the statement "an oxidation and a reduction very frequently go together", in § 474. Here is a case where there are two reductions.

480. Hydrogen peroxide solution is usually sold with a statement as to how much oxygen it will liberate. Thus "10 vols." on the bottle would mean that every litre of the solution can liberate 10 litres of oxygen. The solution must be kept corked or stoppered. If a glowing splinter is introduced into the neck of a bottle of the peroxide which has been standing for some time, it will be rekindled, showing that decomposition has been taking place.

Hydrogen peroxide is used as a disinfectant, though its efficiency for this purpose does not appear to be great. It is, however, a very good cleanser of wounds.

481. The formula is written H_2O_2 . That it contains nothing but oxygen and hydrogen is easily verified, since it yields only oxygen and water when it decomposes.

By taking a pure specimen and measuring the amount of oxygen it gives off, it can be proved that when 16 gm. of oxygen are evolved 18 gm. of water are left. That is to say the proportion of oxygen to hydrogen is just twice as great as in water. Any formula such as HO , H_2O_2 , H_3O_3 , etc., agrees with this. The formula H_2O_2 can be proved to be right by the freezing-point method.

482. This method of proving the formula involves the troublesome process of preparing a pure specimen of the peroxide. It is interesting to consider how far we can get towards deducing the formula without a pure specimen, but with a water solution only.

Suppose a specimen of the diluted peroxide is frozen and the freezing-point noted. If the freezing-point is 1.85°C . below that of pure water, then the solution contains 1 grammic-molecule of the

peroxide per litre. In any actual case by observing the freezing-point and applying Blagden's Law the solution can be diluted till the depression is 1.85°C. , and thus a solution containing a gramme-molecule of hydrogen peroxide in a litre can be obtained. This can then be heated and the oxygen collected and measured, its volume at N.T.P. calculated and so its weight deduced. It is found by experiment to be 16 gm. This is the known atomic weight of oxygen. Thus a gramme-molecule of the peroxide gives off a gramme atom of oxygen. Hence every molecule gives off one atom of oxygen, leaving water behind. So the formula must be $(\text{H}_2\text{O})_x\cdot\text{O}$, where x is a whole number. This is as far as we can go without a pure specimen. The simplest formula this permits, when $x = 1$, is H_2O_2 . It is well worth while trying to see exactly why this formula cannot be proved more definitely by the freezing-point method without preparing a pure specimen. It will be remembered that the freezing-point method hinges on the fact that the depression depends upon the number of molecules present in a litre and not on their weight or kind. Suppose, then, the formula were H_2O_3 . Now imagine that by some fanciful process each molecule were to combine with another molecule or two of water. The amount of oxygen liberated on heating would be unchanged; also the number of molecules present would be unchanged. So there would be no change in either of the observed quantities—the amount of oxygen liberated and the depression of the freezing-point. Hence the method will not settle what the value of x is. It does, however, rule out the formula HO . The only value of x which agrees with the percentage composition is H_2O_2 . Directly we appeal, however, to the percentage composition, we are making use of information derived from an experiment on a pure specimen of the peroxide.

483. Hydrogen peroxide added to a dilute solution of potassium dichromate, acidified with a drop or two of sulphuric acid, produces a marked and characteristic blue colour due

to the formation of per-chromic acid. It is unstable and the colour rapidly disappears. It is more permanent if a layer of ether be added, the blue compound dissolving in the ether (see § 684).

484. The peroxide is usually described as acid to litmus, though this cannot be verified in an ordinary dilute specimen as such specimens contain traces of the acid used in their preparation.

485. Ozone. It was long ago noticed that a curious odour was developed in the presence of an electrical machine at work. This is due to the production of a new and very remarkable substance in the air, ozone. It may be produced by the simple apparatus shown in fig. 37, which consists merely of a piece of

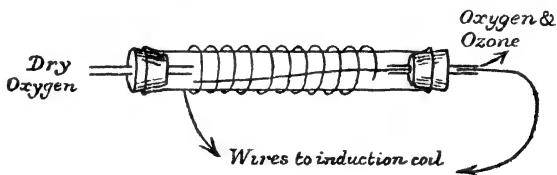


Fig. 37. Preparation of Ozone.

glass tubing with one piece of platinum wire inside along its length and another coiled round the outside. A slow stream of oxygen is passed down the tube and the two wires are connected to the terminals of an induction coil. A silent electric discharge passes across the space between the wires and the oxygen which issues from the tube has acquired the smell characteristic of ozone. It will be seen that the substance has been made from oxygen and nothing else, so that it must be an allotropic modification of oxygen, just as diamond is, for example, of carbon. Unlike diamond, however, ozone is very unstable and turns back to ordinary oxygen on heating. A certain amount of ozone is produced during the slow oxidation of phosphorus in moist air.

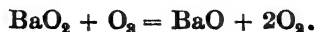
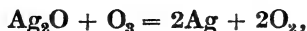
486. Ozone is soluble in turpentine; oxygen is not. This property is used to find the molecular construction of ozone. A volume of "ozonised" oxygen is produced and is divided into two equal parts. One part is heated and then cooled to the original temperature and pressure. The increase in volume on cooling is noted. The second portion is treated with turpentine which dissolves the ozone. The decrease in volume due to the withdrawal of the ozone is measured. We now have sufficient information to find a formula for ozone. An example will make this clear.

Suppose each portion of ozonised oxygen measures 100 c.c.

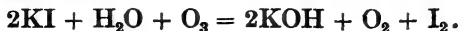
Suppose the first portion after heating occupied 103 c.c. and the second after treatment with turpentine occupied 94 c.c. Clearly 94 c.c. is the volume of oxygen which remained unaltered throughout the experiment in each case. Clearly, too, 100 c.c. - 94 c.c., i.e. 6 c.c., was the amount of ozone present and 103 c.c. - 94 c.c. or 9 c.c. was the volume of an equal amount of ozone after it had been turned back again into ordinary oxygen. So 9 c.c. of oxygen are produced from 6 c.c. of ozone. This means that 1 molecule of ozone produces $1\frac{1}{2}$ molecules of oxygen; the molecular formula of ozone is therefore O_3 .

If this view is true, ozone would have a density 24 times that of hydrogen. This has been verified independently by experiments, which were not at all easy, on its rate of diffusion (see chap. xx).

487. Ozone is much more active than ordinary oxygen. It produces a scum of oxide on the surface of mercury and at once oxidises lead sulphide to lead sulphate, as does hydrogen peroxide. The action of ozone on some oxides will recall the action of hydrogen peroxide on silver oxide. For example, the actions represented by the two following equations take place readily:



On potassium iodide solution the action of ozone is expressed thus:



The liberated iodine is brown in colour but can be recognised more easily and in smaller quantities by the blue colour it produces with starch. Blotting paper soaked in starch and potassium iodide solution is useful, when moist, as a test for ozone and for certain other oxidising agents, nitrogen peroxide, for example. Like many oxidising agents ozone has bleaching properties. It is useful as a disinfectant. The odour of ozone is noticeable on the London "tubes" and the New York subways. The gas is produced not merely by the electrical machinery of the trains; ozone is manufactured by the management to keep the air purified. The ozone in the air boasted of by those interested in the development of sea-side resorts is probably apocryphal.

488. Potassium permanganate (see chap. LV). In the course of our work several compounds of manganese have been met with, all of which are obtained from the black oxide, manganese dioxide. This is of fairly common occurrence as a mineral and in this form it is known as *pyrolusite*. It was used in the preparation of chlorine and left a residue of manganese chloride, MnCl_2 , a slightly pink salt, and the reader has no doubt gathered, and gathered correctly, that manganese is classed as a metal. What exactly this implies will be discussed in more detail in chapter XXXII. Being a metal its salts yield positive ions in solution and the common salts of the metal manganese—the chloride, the sulphate and so on—can be derived from the basic oxide—manganese oxide, MnO —by dissolving this oxide in the appropriate dilute acid.

489. There is, however, another class of manganese compound in which the manganese appears in the salt in the negative ion; in which, in fact, manganese appears to act as a non-metal and to produce acid-forming oxides. The acids themselves are unstable and unimportant, but the corresponding salts are of

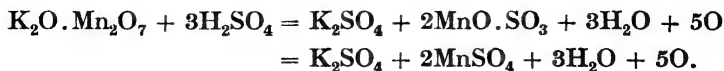
great interest and usefulness. The acid-forming oxides of manganese contain a larger proportion of oxygen than manganese oxide, the common basic oxide. There are two common classes of these salts, viz. the manganates, e.g. potassium manganate, K_2MnO_4 , and the permanganates, e.g. potassium permanganate, $KMnO_4$. Writing these in the convenient way explained earlier in the chapter, to show how they are related to the oxides, we have

manganese sulphate: $MnO.SO_3$,
 potassium manganate: $K_2O.MnO_3$,
 potassium permanganate: $K_2O.Mn_2O_7$.

The reader is again reminded that the formulae are written in this way for convenience only. They suggest the relationship of these salts with certain oxides, but must not be taken to assert that the molecule of the salt is actually constructed of these oxides. Potassium permanganate, in rather small crystals of an unforgettable colour, between crimson and purple with a green sheen, is one of the familiar substances of any laboratory.

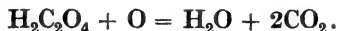
490. If manganese dioxide be heated with caustic potash and potassium nitrate, a green mass is formed which dissolves in water yielding a green solution of potassium manganate, K_2MnO_4 , and this gradually reddens on exposure to the air as it oxidises to the permanganate, $KMnO_4$. Or the permanganate can be produced directly by heating manganese dioxide with potassium chlorate and potassium hydroxide.

491. An acidified solution of potassium permanganate is an excellent oxidising agent. The action will easily be understood by looking at the following equation, in which the permanganate is expressed as a compound of oxides:

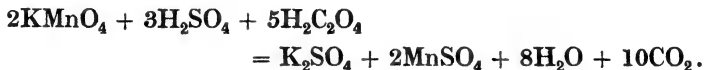


It should be noticed that the equation as it stands is incomplete

and might, without a caution, be misleading. Potassium permanganate and dilute sulphuric acid do not actually give off oxygen. But if there is a readily oxidisable substance present, then that substance will be oxidised, and the equation given shows, in all ordinary cases, how much oxygen is available for this purpose. Thus the equation expresses the fact that for each two molecules of KMnO_4 which take part in the reaction five atoms of oxygen are available for oxidising, and bearing this in mind, the action in any real case can usually be foretold without difficulty. The permanganate, for example, can be used to oxidise oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, to water and CO_2 . The equation for this stage is



Hence the action of potassium permanganate on oxalic acid is expressed by the equation



Such equations look very complicated; but they need not be remembered as, after a little examination of the principles on which they are based, they can easily be worked out. The above equation is important. The action is attended with the disappearance of the colour of the permanganate and this, if the permanganate be added drop by drop, serves to mark exactly the end-point. Thus the action may be made the basis of a quantitative titration, the permanganate serving as its own indicator.

492. The permanganate in presence of acid yields oxygen with hydrogen peroxide, the action resembling that of the peroxide on silver. The reader will have no difficulty in constructing the equation.

493. Potassium dichromate (or bichromate; see § 163) is another important oxidising agent. The commonest raw material of chromium salts is the mineral chromite, or chrome ironstone, a compound of the oxides FeO , ferrous oxide, and

Cr_2O_3 , chromic oxide. When this is roasted in air, with potassium carbonate, lime being added to make a suitably porous mass, the chromium oxide is converted into a yellow solid, potassium chromate, K_2CrO_4 , thus:



The potassium chromate made in this way can be dissolved out and obtained as yellow crystals, easily soluble in water. On treating with an acid this chromate is converted into the dichromate thus:



The potassium dichromate thus obtained can be crystallised out in the form of the familiar large orange-red crystals.

The formula of potassium dichromate can be written as if the salt were a compound of two oxides, thus: $\text{K}_2\text{O} \cdot 2\text{CrO}_3$.

494. It should not be undue optimism to expect the student to work out the equation for the oxidising action of a dichromate for himself. But perhaps the following equation had better be supplied to help him. It can be compared with the similar equation for the permanganate:



Suppose, for example, we want to make use of this equation to write down what happens when potassium dichromate oxidises ferrous chloride to ferric chloride in presence of dilute HCl . The 3O at the end of the equation gives the clue. This will act upon six molecules of HCl to yield six atoms of chlorine which will oxidise six molecules of ferrous chloride. Hence the final equation will be



Of the fourteen molecules of HCl , eight take the place of the $4\text{H}_2\text{SO}_4$ in the previous equation, and the other six are the calculated amount oxidised by the three atoms of oxygen.

495. Potassium dichromate is somewhat less active than the permanganate. The latter, for example, will liberate chlorine from strong hydrochloric acid without heating; the dichromate requires to be warmed. Also the well-marked colour change when the permanganate is reduced is an immense advantage when titrating. So the permanganate is the more useful of the two in the laboratory.

Chapter XXXI

FLAME

496. If the substances taking part in a chemical action become so hot that they emit light, they are said to be "incandescent". A mass of hot gas is called a "flame". How hot the gas has to be before it merits the title is just a matter of convenience, but for all practical purposes a "flame" may be recognised by its power of setting fire to ordinary combustible objects such as a match or a piece of paper.

497. Flame and incandescence need not be associated with chemical action. They require for their production energy, and that energy is frequently due to chemical action though it need not be. Thus in an electric-light bulb the filament is kept incandescent by energy from an electric source. The incandescence of the sun is due to its internal heat energy and is not produced by combustion. Also the "flames" visible in the sun's corona during an eclipse are masses of gas heated from the same source. These are flames without combustion. Note, in passing, that there are no "flames" over a volcano in eruption. There is usually an incandescent mass inside the crater; there is also a cloud of steam and other vapours over the top which glows luridly by the reflected light from the interior. The imagination of the poet or the journalist supplies the "flames" as a finishing touch.

498. The flame produced by the combustion of gases may be dazzlingly incandescent or "luminous", as in the case, for example, of acetylene burning in air. Or it may be practically invisible, as is the flame of pure hydrogen or of coal gas burning in a Bunsen burner with the appropriate air supply. Many a coat sleeve has come to grief in the laboratory from this cause.

To produce light from a non-luminous flame is frequently a problem of practical importance. One does not have to be very old to remember the days before the common use of electric light, or, earlier still, the time when the incandescent gas mantle had not been invented. At that period coal gas was commonly burnt in a "fish-tail" burner, without any admixture of air. The result was a flat luminous flame with a slightly yellow light. The admission of air into the pipe through a hole like that at the base of the Bunsen burner increased the temperature of the flame but decreased the light. The incandescent mantle was then introduced. These mantles will be quite familiar to the reader. They contain the oxides of two rare metals, thorium and cerium, mainly thorium. These become white hot in a Bunsen flame and provide a very satisfactory light by their incandescence. In limelight a cone of lime is used for a similar purpose. This has been referred to in chap. iv.

499. The structure of flame has been examined in great detail. For our present purpose the following considerations will suffice.

The diagram of the ordinary Bunsen burner is seen in fig. 38. The gas issues from a jet at the bottom of the tube and draws a supply of air through the holes at the side. The gas and air become mixed as they pass upwards and can be burnt with a feebly luminous flame at the top.

A normal Bunsen flame consists of three regions:

1. A hollow space of unburnt gas on the inside.
2. A more luminous cone.
3. An outer mantle.

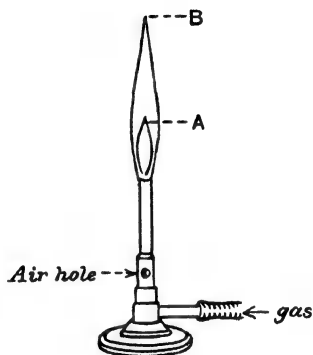


Fig. 38. Bunsen Burner.

A vigorous combustion takes place at the surface of the cone 2, where the coal gas burns in the air which was drawn through the holes at the bottom. A less vigorous combustion takes place in the outer mantle between the gases produced by the burning at the inner cone (together with any unburnt gas) and the oxygen of the air.

The air-hole at the base must be regulated so that the right quantity of air is admitted. If there is too much air, the burner "strikes back" and burns at the base. If there is not enough, the flame becomes luminous. There is no doubt that this is due to the formation of carbon in the flame. Probably this is formed by decomposition of the hydrocarbons; as far as can be ascertained it is not due to the combustion of the hydrogen in preference to the carbon. The presence of carbon in the luminous flame may be shown by introducing a piece of cold porcelain—e.g. a saucer—which immediately becomes coated with soot.

500. A Bunsen flame may be used for reducing. Considered from the point of view of the air, the oxidation of the gas involves the removal of oxygen from the air. If a substance capable of being reduced be placed on the inside of the flame, the combustion may be made to proceed partly with the help of the oxygen in this substance. In this way, for example, red lead, Pb_3O_4 , may be reduced to metallic lead. This reduction is more easily effected if the air-hole is partially closed. It will readily be seen that a diminution of the oxygen supply from elsewhere will encourage the use of the oxygen in the red lead. A very small quantity of lead oxide must be used. It is placed at the point *A*.

501. A Bunsen flame may also be used for oxidising. On the outside of the flame all the gas has been burnt. There is no tendency for the gas there to use up the oxygen in a piece of red lead or other reducible substance placed there. The effect of putting an oxidisable substance at *B* is to heat it strongly in the presence of air, and thus to oxidise it.

502. The reducing and oxidising powers of a flame are best put into practical use by the aid of a blowpipe. A simple blowpipe is merely a tube with a fine bore, through which air may be blown from the mouth into a flame. The jet at the end of the tube is bent round at right angles to the main tube. It is helpful to use also a piece of tube as shown in fig. 39. This is slipped inside the Bunsen burner. It cuts off the air supply. The top is flat and cut at an angle. The gas, lit at the top, gives a flat luminous flame. The point of the blowpipe is rested at *D* and air blown in. With a little practice it is not difficult to blow continuously through the blowpipe for five minutes or more at a time. The blowing is done by the pressure from the cheeks which are distended, while the ordinary in and out respiration goes on from the lungs through the nose. This is a simple accomplishment which anyone can learn, and its acquirement gives a peculiar satisfaction, such as is experienced by the beginner when he first learns to ride a bicycle or to swim.

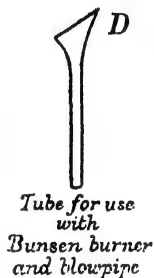


Fig. 39.

Sometimes a mechanical blowpipe is used, the air being forced in by some artificial means such as a foot-bellows.

By means of the blowpipe either the reducing or oxidising part of a flame can be conveniently directed on to a small piece of anything, and this is commonly done in examining many substances. The way they behave in the oxidising and in the reducing flame often gives a valuable clue as to their nature and composition. The student will learn more about this when he tackles the important subject of practical analysis (see §§ 694 and 700).

Chapter XXXII

METALS

The Alkali Metals: Sodium and Potassium.

The Alkaline Earth Metals: Calcium, Strontium and Barium.

503. The term **metal** is in ordinary use, and in chap. v we took the first step towards borrowing this simple everyday word and giving it a more precise scientific meaning. From that point we worked up to the idea in chaps. XXVIII, XXIX of metals as being capable of existing as positive ions, and by now the student should have a much more vivid idea of what a metal is and how it behaves chemically than when he began.

It is worth noting that the properties which make metals so valuable in ordinary life—their hardness or durability or the ease with which they can be worked or their ornamental beauty—are not those which are of special interest to the chemist. The most obvious property of a metal is its shiny surface (hence the phrase “metallic lustre”). This property is usually absent if the metal is finely powdered. Metals are also distinguished by being good conductors of electricity, silver being the best conductor known with copper a very useful second. They are, too, good conductors of heat. But we have seen in chap. xv that the property which distinguishes them as a group for the chemist is their power of forming basic oxides or hydroxides. They form salts with acids, and although not every metal forms a salt with every acid (for example, the reader will recall that there appears to be no stable carbonate of aluminium), yet it is fairly safe to say that every metal forms a sulphate and a chloride.

To sum up, then:

504. Metals, *physically*, have shiny surfaces in bulk and are good conductors of heat and electricity. They are *malleable*—i.e.

can be hammered into thin sheets—and are *ductile*—i.e. can be drawn out into thin wire.

Chemically they form basic oxides and so with acids yield salts, i.e. compounds in which a metal has taken the place of the hydrogen of an acid. When a salt is dissolved in water the metal appears positively charged as a “kation”.

505. Non-metals, on the other hand, are for the most part opposite to metals in their properties. They do not generally have a metallic lustre, they are as a rule bad conductors of heat and electricity and are neither malleable nor ductile.

Chemically their oxides are acid-forming. Some of the non-metals form acids by combining with hydrogen alone. Where a non-metallic oxide forms an acid with water, the oxide is called the “anhydride” of the acid. Thus SO_3 is sulphuric anhydride. When a salt is dissolved in water the non-metal appears in a negatively charged ion, the “anion”.

These are the main distinctions. They must be read a little critically, in the light of knowledge acquired. NH_4 , for example, forms a well-marked positive ion, though it contains no metal. $\text{K}_4\text{FeC}_6\text{N}_6$, potassium ferrocyanide, yields a negative ion, FeC_6N_6 , which however includes the metal iron. Although this ion contains iron, the reader is again reminded that potassium ferrocyanide does not show any of the reactions which are usually associated with compounds of iron (see § 460). Some elements, notably arsenic and antimony, are on the border line. They are neither definitely metals nor definitely non-metals and regularly occur in the basic part of some salts and in the acidic part of others.

506. Sodium and Potassium. Turning now to look a little more closely at the metals individually, the first to occupy our attention will be the so-called “alkali metals” of which sodium and potassium are by far the commonest and most important. Compounds of sodium and potassium are very much alike in their chemical properties. If the properties of sodium and its compounds are carefully noted, it will suffice, for potassium, to

point out in what respects its compounds differ from those of sodium.

507. Sodium compounds are very common in nature. Vast quantities of sodium chloride are found in sea water and in the various deposits of salt, such as the salt mines in Cheshire and Poland. Potassium compounds, however, appear to be quite as plentiful though less accessible. Potassium exists in plants and the carbonate may be extracted from their ashes with water—hence the name, a latinised form of “potash”. Since potassium is found in plants, it is clear that potassium salts must be supplied to plants; they are therefore a necessary ingredient of many fertilisers. This gives a commercial value to mineral potassium salts, which are, however, none too common in a readily available form. The principal source is the deposit at Stassfurt in Germany, where a salt with the formula $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, coloured with iron and known as “carnallite”, is very abundant. A great deal of the potassium in nature is found in felspar, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. This is one ingredient of granite, syenite and a number of other rocks. Research is at present going on with a view to making the potassium in such compounds available in quantities at reasonable prices.

The fact that sodium salts are cheaper than those of potassium is apt to give the impression that they are more abundant in nature. By weight, they appear to be about equally widespread. It may be noted that, this being so, there are more atoms of sodium; the atoms will be present in the ratio of about five to three.

508. A future source, and a very important one, of potassium salts is almost certain to be the Dead Sea. This sea contains vast quantities of NaCl , KCl and MgCl_2 in addition to bromides and smaller quantities of other salts. On evaporating the water of the Dead Sea, the NaCl , the least soluble ingredient, crystallises first, the next crop of crystals being carnallite and containing the bulk of the potassium. The whole process is simplified by the

fact that there are practically no sulphates present. The development of this vast supply of potash—one enthusiast has estimated the weight present as 1,800,000,000 tons—will be of interest to Britons as it will mean a steady supply within the Empire. This will break what was practically a German monopoly both of potassium salts and of bromides. The reader is advised to keep his eye on the newspapers for further developments in this matter, which is developing apace. Negotiations for the concession to work the Dead Sea salts have recently been concluded. It has been decided by the Palestine Government to build a harbour at Haifa and an electric railway is projected from there to the Dead Sea. The Palestine mandate looks like being of far greater importance than originally appeared.

509. The free metals, sodium and potassium, are still obtained by the method originally used by Sir Humphry Davy over a century ago, namely, by passing an electric current through the fused dry hydroxide. Other salts—e.g. the chloride—may be used, but the hydroxide is the most satisfactory compound for the purpose. The electrodes are of iron. The metal appears at the kathode, together with hydrogen, oxygen being evolved at the anode. The anion is OH^- , which when liberated yields oxygen, thus: $4\text{OH}^- = 2\text{H}_2\text{O} + \text{O}_2$. This produces water and it is the subsequent electrolysis of this water which gives hydrogen at the kathode. Sodium and potassium can also be extracted from their carbonates by reduction with carbon at a high temperature. This method used to be employed a great deal, but now Davy's original method has come into its own again.

510. The melting-points of the metals are low—sodium $92^\circ\text{C}.$, potassium $62^\circ\text{C}.$ —and at ordinary temperatures they are waxy solids, easily cut with a knife, and with a bright surface which rapidly tarnishes in air. Being so very readily oxidised they are kept under naphtha—not water (see § 46, though it is to be hoped that this reference is unnecessary). A mixture of sodium and potassium is liquid at ordinary temperatures, an example of

what is commonly the case, that the addition of one metal to another lowers its melting-point, so that it is usually possible to make from two metals a mixture or "alloy" with a melting-point lower than that of either of the pure metals. This liquid alloy of sodium and potassium has been suggested as a substitute for mercury in thermometers. A little reflection will serve to convince the reader that mercury has not much to fear from the competition. A rare alkali metal, much like sodium and potassium and called "caesium", has a melting-point as low as 26° C.

511. Common salt, NaCl , is the most important compound of sodium. It is important both for its own sake and also as the raw material from which other compounds of sodium are made. Two of the latter, sodium hydroxide and sodium carbonate, are of first-rate industrial importance.

Sodium hydroxide is second only to sulphuric acid among the chemicals used in technical processes, and its manufacture is carried out on a very large scale. Formerly it was made by heating sodium carbonate with lime and water:



Here the calcium carbonate is insoluble and the slaked lime sufficiently soluble to keep up a supply of Ca ions and of OH ions and hence the action takes place according to the equation, the insoluble carbonate being easily removed.

The reaction, however, is reversible. Excess of lime is used to promote the forward action, but even so some of the sodium carbonate remains as an impurity in the sodium hydroxide. This can be separated out by crystallisation, and can then be added to a fresh portion of carbonate and worked up with more lime. If the solution of carbonate used is sufficiently dilute, however, the reverse action is inappreciable.

512. Nowadays, however, the hydroxide is made almost entirely by the electrolysis of the chloride in strong solution. Compare this with the manufacture of metallic sodium, where the

fused dry salt is used. The anode is of carbon and the kathode of steel. In the electrolysis of a chloride a metallic anode is impossible, even platinum being dissolved by nascent chlorine. The action may be considered in stages thus:

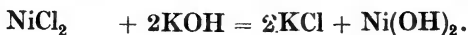
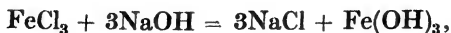
(1) NaCl in water gives ions of Na and Cl.

(2) The Na ions travel with the current to the kathode and the Cl ions against it to the anode.

(3) The Na ions would, in absence of water, yield metallic sodium, but in presence of water they yield hydrogen, which is liberated, and NaOH, which remains in solution. The Cl ions yield chlorine at the anode (see § 176).

513. Both the hydrogen and the chlorine are very useful by-products of the action (see §§ 50 and 177). In a common form of the apparatus the steel kathode takes the shape of a vessel punctured all over with little holes like a colander (to be seen in any kitchen) and lined inside with asbestos. The hydroxide formed passes through the holes in the kathode and is collected as it drops out. It can be concentrated and cast into sticks.

514. Caustic soda is very deliquescent (see § 88). The addition of a little NaOH to water imparts a soapy feeling to the water. Caustic potash, KOH, has very similar properties, and for most common chemical reactions either substance may be used with complete indifference. The addition of a solution of either hydroxide to a metallic salt often yields a precipitate of the hydroxide of the metal, e.g.



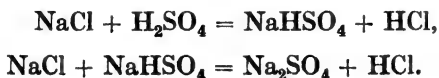
Nickel chloride

515. Sodium carbonate, familiar in the kitchen as “washing soda”, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (see § 88), is another important derivative of common salt. Formerly it was extracted directly from the ashes of seaweeds or seashore plants just as potassium carbonate

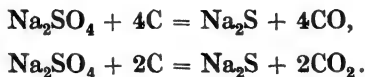
was from land plants. From this source a crude carbonate termed "barilla" was put on the market. Large natural deposits occur at Magadi in British East Africa. This native soda may prove a serious rival to that manufactured by the processes outlined below.

The manufacture of sodium carbonate is now an important technical process. There are two chief methods, the older one, the Le Blanc process, being now supplanted by a later process, the Ammonia-soda or Solvay process. Both processes start with common salt as the source of the sodium.

516. Le Blanc process. The chloride is heated with sulphuric acid and so converted into the sulphate, thus:



The sodium sulphate is heated with limestone and coke, and the action may be represented thus:



(The amount of coke present will decide whether the oxide of carbon is mainly monoxide or mainly dioxide. In practice there is usually excess of coke.)



The sodium carbonate is dissolved out with water and can be crystallised as the hydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, the ordinary soda of commerce and the kitchen. (See Plate VII.)

517. Solvay process. This, the newer process, is a very cheap and interesting way of making sodium bicarbonate, NaHCO_3 . This salt is somewhat less soluble in water than most compounds of sodium. The salt is produced by the interaction of water, ammonia, common salt and carbon dioxide. A convenient way

conditions are fulfilled by the carbon dioxide. Cooling is also promoted by passing cold water over the outside of the tower, or through coiled tubes within the tower.

A pasty mass collects in the tower. It is drawn off at intervals and filtered, the bulk of the bicarbonate being thus separated out as fine crystals.

The carbon dioxide is obtained by heating chalk or limestone:



If the lime produced by this action is heated with the ammonium chloride produced in the tower, the ammonia is reproduced:



Thus the ammonia is restored for further use, and though, of course, there will inevitably be a certain waste and leakage, it is used up but slowly. The waste product is calcium chloride which is of little value. The chlorine of the sodium chloride is thus lost. However, the raw materials of the action—limestone, salt and the fuel for decomposing the limestone—are none of them expensive, and hence the retail price of washing soda in an ordinary shop is less than a penny a pound. This cheapness is partly due to the fact that the crystals sold, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, contain such a very large percentage of water—nearly twice the actual weight of the carbonate, in fact. If the salt is manufactured for export, it is sent out as the anhydrous salt, to avoid paying freight on the water of crystallisation. The crystals when left to themselves in the open air “effloresce”, i.e. they give off water, and crumble to a white powder of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (see § 88).

It is worth noting that potassium carbonate cannot be produced by any process like the ammonia-soda process, as the latter depends upon the comparative insolubility of sodium bicarbonate, and in this respect the sodium salt differs from the potassium salt.

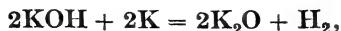
518. A mixture of the carbonates of sodium and potassium has a lower melting-point than that of either carbonate by itself. Such a mixture is useful as a "flux". It is sometimes necessary to heat two solids together in intimate contact. In such a case they are often mixed with a flux and the whole mass heated above the melting-point of the flux which thus acts as a solvent, and by dissolving one or both of the solids brings them into intimate contact and promotes chemical action.

519. A number of sodium and potassium salts have already been introduced to the reader, and he may like to pause here and recollect what he knows about sodium sulphate ("Glauber's salt"), sodium nitrate ("cubic nitre" or "Chile saltpetre"), sodium borate, sodium silicate, potassium nitrate, potassium chlorate, potassium hypochlorite, potassium dichromate, potassium permanganate, potassium bromide, potassium iodide, sodium thiosulphate, the phosphates of sodium and any other sodium or potassium salts he may have met with.

520. Metallic sodium in presence of water acts as a reducing agent. It should be obvious why this is so. The metal dissolves in mercury to form an "amalgam". It is the custom to refer to an alloy containing mercury as an "amalgam". This is just a peculiarity of wording. There is no very scientific reason why a special term should be used for alloys of mercury. Sodium amalgam acts on water to form NaOH and mercury. It is a more practical reducing agent than pure sodium as it is less active and so more manageable.

521. Two oxides of sodium, Na_2O and Na_2O_2 , are of interest, and two oxides of potassium, K_2O and K_2O_4 . The oxides Na_2O and K_2O might, from the laws of valency, be expected to be the commonest oxides. This is scarcely true. If sodium is burnt with plenty of oxygen the oxide formed is the peroxide Na_2O_2 , and under the same circumstances potassium yields K_2O_4 . The monoxide, with an admixture of peroxide, is produced if sodium is oxidised with a very limited supply of air and the temperature

is not allowed to rise. These oxides are best produced by heating the hydroxide with the metal in the absence of air:



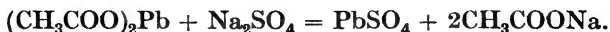
with a similar equation for sodium. The monoxides combine vigorously with water, yielding the hydroxides.

The dioxide of sodium (oxone; see § 31) dissolves in *cold* water without change. With warm water it yields caustic soda and oxygen and so is a very useful oxidising agent (see §§ 599 and 681). Both Na_2O_2 and K_2O_4 are yellow powders; their appearance, the ease with which they yield oxygen with water, and the soapy "feel" they produce in the water make them easy to identify.

522. Sodium salts colour a colourless Bunsen flame yellow, potassium a delicate lilac, and this is the simplest way of distinguishing between them.

523. It has been mentioned repeatedly that salts of sodium and potassium are usually soluble in water. There are a few exceptions to this. Potassium perchlorate, KClO_4 , is very sparingly soluble; potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, and potassium platino-chloride, K_2PtCl_6 , are practically insoluble. Among sodium salts, the best known insoluble salt is sodium hydrogen pyroantimoniate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$. "Permutite" (sec § 235) is another.

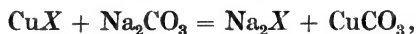
524. But why is the fact that certain salts are or are not soluble in water of any particular importance? There is a very real point in this. If an insoluble salt is formed from two soluble ones, it is deposited as a precipitate. For example, if sodium sulphate solution be added to a solution of a lead salt (e.g. lead acetate $(\text{CH}_3\text{COO})_2\text{Pb}$), there at once appears in the solution a white precipitate of lead sulphate:



This precipitate can be filtered off and in this way all the lead removed. So any one ion can be removed from a mixture if it

can be made to enter into an insoluble salt and so be precipitated. In analysing a mixture this is often a matter of considerable importance. Again, the mere fact that a precipitate forms at all may give information as to what substances are present. Looking back at the example just given, it can be said that if a soluble sulphate be added to a solution and a white precipitate is formed, then there is a probability that lead is present. Or is it perhaps barium? At any rate, the metal is marked down as one of a short list and then further tests are applied to settle more definitely which it is (see §§ 701 and 702).

525. The solubility of the sodium and potassium salts is thus a very valuable property. Much of the testing of substances depends upon the formation of precipitates; since sodium forms practically no precipitates, its presence does not interfere with such testing. For example, suppose a salt of copper which is soluble in water is being examined in order to find out what acid radical is present. Let us call the copper salt CuX . Suppose sodium carbonate added to the solution. There will be a precipitate of a basic carbonate of copper, thus:



some of the CuCO_3 decomposing thus:



(see § 166). If now the precipitate be filtered off, there remains in solution Na_2X , which can be examined for the acid radical X with the assurance that the sodium is not likely to interfere with the reactions by producing unwanted precipitates, as the copper might easily have done. Since all nitrates are soluble in water, —NO_3 serves a somewhat similar purpose among acid radicals (see § 632).

526. It will now be clear why, in a laboratory, so many of the salts are salts of sodium and potassium. Generally speaking, if a salt is stocked for the sake of the acid radical which it contains,

it will probably be kept as the sodium or potassium salt; if it is kept for the sake of the metal, it will probably be a salt which is soluble. It is worth noticing the economic aspect of this. Potassium is considerably more expensive than sodium. If then, for example, a soluble carbonate is wanted, sodium carbonate will be much cheaper. For compare the formulae Na_2CO_3 and K_2CO_3 . A reference to the atomic weights will show that the first contains 46 gm. of sodium to 60 gm. of CO_3 and the latter 78 of potassium to 60 gm. of CO_3 . Hence 1 gm. of the radical CO_3 is contained in a larger weight of the potassium salt than of the sodium salt. So both the extra weight required and the extra cost of the potassium make the potassium salt less economical. But in such a salt as NaI or KI , the iodine is so expensive that the cost of the sodium or potassium is trifling by comparison. An ounce, say, of KI contains less iodine than an ounce of NaI , and hence potassium iodide is cheaper per ounce than sodium iodide. From the chemist's point of view this difference is of little moment. It would suit him just as well to pay more per ounce for the sodium salt. He would get just as much combined iodine for, say, a shilling. As a matter of fact the bromides and iodides usually stocked are the potassium salts. The decisive reason for preferring potassium iodide to sodium iodide is that the latter is deliquescent but the former is not. As the iodide is chiefly used in the laboratory for quantitative work, the potassium salt is very much more suitable than the sodium salt.

If the public were offered pure potassium permanganate and sodium permanganate at the same price per ounce, they would probably think the former a better bargain if they realised that potassium was dearer than sodium. Indeed, the reverse is the case, as the reader should be able to see for himself. Again, the reason for preferring potassium permanganate to sodium permanganate, both for quantitative work in the laboratory and for use in the household as a disinfectant, is that the sodium salt is deliquescent but the potassium salt is not.

527. The alkaline earth metals. Calcium, strontium and barium, the alkaline earth metals, form a well-defined family group, resembling each other as closely as do chlorine, bromine and iodine.

528. Calcium is, in combination, an exceedingly plentiful metal in nature. The abundance of the carbonate has been stressed in chap. XVIII. The phosphate and sulphate have also been referred to, and the chloride, very soluble and very hygroscopic, has been met with as a drying agent. It is also a common end or waste product in the large-scale manufacture of chemicals (e.g. Na_2CO_3 and NaHCO_3 , see § 517). Most of the facts about calcium compounds which the reader need know have already cropped up in connection with other substances, and he may well stop here for a moment and recollect all the calcium compounds he has met with and what he knows about them.

The metal itself is worth a little notice. The older method of preparing it, due to Moissan (see "Fluorine"), was by heating calcium iodide with sodium:



The more modern method is similar to Davy's method of preparing sodium, i.e. by electrolysis of the fused chloride, a little calcium fluoride being added as a flux.

The metal calcium is harder than sodium and less active. It has, too, a much higher melting-point ($810^\circ \text{C}.$). (For calcium compounds, see §§ 205, 215, 230–236, 364, 376, 417, 698 and 702.)

529. Strontium and **barium** are very similar to calcium in general properties. Strontium salts colour a Bunsen flame a bright crimson, barium a vivid green. The salts of these metals, notably the nitrates, are hence of use in the manufacture of fireworks. Calcium salts colour a flame an orange colour. These flame colours are useful as confirmatory tests for the metals.

530. Barium sulphate has a useful application in medicine. When the stomach or intestine is examined by X-rays the tissue

is too soft to make a clear photograph possible. So the patient is first given a large draught up to about a quart of sugar solution containing plenty of finely divided barium sulphate in suspension. This coats the inside of the alimentary canal which can then be photographed sufficiently clearly to enable the doctor to form an opinion about it. In this way, for example, ulcers in the stomach or intestine can be located. Barium sulphate is also used as a principal ingredient in some kinds of white paint.

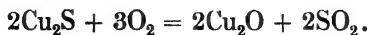
Chapter XXXIII

THE INDUSTRIAL METALS (NON-FERROUS)

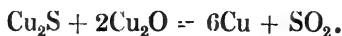
531. Of the remaining metals, there are several which must claim our attention owing to their great importance in everyday life. Of these copper, zinc, tin, lead, iron and—a metal which has leapt into prominence in the lifetime of many of us—aluminium come to the mind at once. Gold and silver—especially gold—are not much studied in elementary chemistry, probably owing to the prosaic fact that though important, largely in connection with currency, they are too expensive to permit of their use in the quantities which are required for the laboratory work of school classes.

532. Copper is occasionally found native—i.e. in a free state. It is more usually obtained from its ores, the commoner ones being the red oxide, or cuprite (Cu_2O , cuprous oxide), the black oxide (CuO , cupric oxide), copper glance (Cu_2S), copper pyrites or “chalcopyrite” (CuFeS_2), malachite (a basic carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) and azurite (another basic carbonate, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$).

533. When there is no sulphur present, the oxide or carbonate is easily reduced to the pure metal by heating it in a blast furnace with coke or coal. If a sulphide ore is used the process is a good deal more elaborate. The essential part of the method consists in heating the sulphide in the air until part of it is burnt to an oxide of copper, thus:



If now a mixture in suitable proportions of the sulphide and oxide is heated, the copper is liberated according to the equation:



In actual practice the process is not nearly so simple and is very much complicated by the presence of iron and other impurities.

534. Copper can be purified electrolytically. The impure copper is made the anode and a piece of pure copper forms the kathode, the two being immersed in copper sulphate solution. As the current passes, the anode dissolves, copper goes into solution and pure copper collects on the kathode. "Electrolytic copper" is regularly quoted on the metal market. (See Plate VIII.)

535. The ordinary appearance of copper will be quite familiar. Pure copper is both ductile, i.e. can be drawn out into a thin wire, and malleable, i.e. can be hammered into thin sheets. Its very low electrical resistance renders it particularly useful for electric wiring. It is permanent in dry air, but under ordinary conditions if allowed to get damp it forms a basic carbonate with the CO_2 in the air. This is the familiar green deposit known as "verdigris". The surface oxidises slightly upon heating in air, but red-hot copper will not decompose steam.

Copper does not replace the hydrogen of acids directly as does zinc. Its actions upon sulphuric and nitric acid have already been described (§§ 345 and 298). With concentrated hot HCl it dissolves slowly to form cuprous chloride, Cu_2Cl_2 . In presence of air this is converted into cupric chloride, CuCl_2 .

536. Pots and pans of copper are familiar objects of the kitchen. The metal is, however, more used in alloys than pure. Of them brass—about 70 per cent. Cu to 30 per cent. Zn, by weight—and bronze—about 90 per cent. Cu and 10 per cent. Sn, but often containing some zinc as well—are the best known.

537. Copper forms two series of compounds, the **cuprous** compounds, in which the metal is *univalent*, and the **cupric** compounds, in which it is *bivalent*.

Cuprous oxide, the red oxide, has already been referred to as a mineral and in connection with Fehling's solution (*q.v.*). Cuprous chloride, Cu_2Cl_2 , can be made by adding pieces of copper

to a solution of cupric chloride and boiling with hydrochloric acid:



The cuprous chloride dissolves in the hydrochloric acid, but on dilution comes down as a white precipitate which can be filtered off. It is unstable in air, being readily oxidised.

538. Cupric compounds. These are the more usual compounds of copper. The black oxide has already been met with several times. It may be prepared by heating the nitrate or carbonate. If it be required to make the oxide from the metal, it is a simple matter to make the nitrate first (see chap. XLII). The oxide dissolves in the common acids to give cupric salts and water.

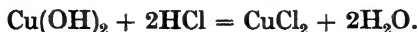
Copper sulphate or blue vitriol is familiar as large blue crystals having the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The anhydrous salt, CuSO_4 , is not blue but white. It is worth noting that many familiar salts differ very much in colour in the anhydrous and hydrated states. For example the word "cobalt" suggests blue at once. But cobalt blue is the colour of certain anhydrous compounds of cobalt. Hydrated cobalt salts and their solutions are usually pink. It will be recollected that the change from white to blue produced in dry copper sulphate on moistening was used in § 87 as a test for water. Very large quantities of copper sulphate are used to spray plants in order to kill off harmful organisms, both animal and vegetable, and for such purposes the solution must be very weak. It is also of practical use in the Daniell electric cell. The solution is slightly acid. This can be explained in the same way as the acid reaction of $\text{Al}_2(\text{SO}_4)_3$ solution (see § 458).

539. Cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, can be made by dissolving cupric oxide in dilute HCl. Or the carbonate can be used instead of the oxide:



The reader is reminded that the usual carbonate of copper is a

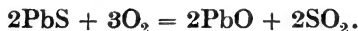
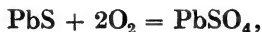
basic carbonate, i.e. it contains $\text{Cu}(\text{OH})_2$ as well as CuCO_3 . So the second equation must be accompanied by another:



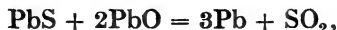
540. Many of the cupric compounds are blue or green; these colours are not exhibited by cuprous compounds. There are cuprous and cupric sulphides (Cu_2S and CuS); both are insoluble and both are black. Copper is often placed in the same group of elements as silver. So far as chemical properties are concerned the resemblance is not striking, but such as obtains is between the cuprous salts and the silver salts. In cupric salts the copper is bivalent and it is not to be expected that they would show any close similarity to the silver salts, silver being univalent.

541. Lead is another metal of great value in everyday life. It is useful, as it is soft and has a low melting-point and so can easily be worked. It is sufficiently permanent in air for practical purposes. The outside tarnishes and forms a film which protects the inside from further action.

The commonest ore of lead is the sulphide, galena, PbS , a shiny black solid. Others are the carbonate or "cerussite", PbCO_3 , and the sulphate or "anglesite", PbSO_4 . To obtain lead from galena the ore is heated with access of air when the following reactions take place:



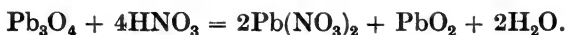
If now the air supply is cut off and more galena added, and the temperature raised, lead is liberated in accordance with the equations:



This process is only workable for very rich ores. For poor ores other methods must be used. A common method is to remove the sulphur by heating the ore with scrap iron, or, what amounts

to the same thing, with iron ore (ferric oxide) and coke. These poorer ores are often very impure and yield appreciable quantities of other metals, notably silver, as by-products.

542. Compounds of lead. The simplest oxide of lead is **lead monoxide**, PbO . This may be made from the metal by melting it and keeping the molten mass stirred to allow free access of air. In this way the lead becomes oxidised to a yellowish powder, PbO , which is known technically as "massicot". "Litharge" is another form of the same oxide. On heating in a current of air to $400\text{--}450^\circ\text{C}$., PbO combines with more oxygen and is converted into **red lead**, Pb_3O_4 , which will be familiar as a paint. If heated still further it splits again into lead monoxide and oxygen. Nitric acid acts upon red lead to form lead nitrate and **lead dioxide**, PbO_2 , thus:



This action will look a little simpler if the red lead be regarded as a combination of two oxides and written $\text{PbO}_2 \cdot 2\text{PbO}$. The nitric acid dissolves the PbO , leaving PbO_2 .

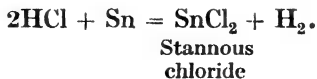
543. Lead hydroxide, $\text{Pb}(\text{OH})_2$, is formed as a white precipitate when a solution of ammonia acts upon a solution of a lead salt. It is slightly soluble in water, giving an alkaline solution which will absorb CO_2 to give lead carbonate. These reactions should be compared with those of $\text{Ca}(\text{OH})_2$.

544. Lead sulphate is a heavy white powder, notable for being one of the few insoluble sulphates. **Lead chloride** is only slightly soluble in cold water, but dissolves far more readily in hot. With sodium carbonate solution, solutions of lead salts yield a basic carbonate, **white lead**, much used as a paint. This, however, is not the way in which it is made commercially. Neither the sulphate nor the chloride being freely soluble in water, one of the most convenient soluble salts of lead is **lead acetate**, $(\text{CH}_3\text{COO})_2\text{Pb}$, also known as "sugar of lead". Lead salts are very poisonous; if taken into the system in small quantities, they

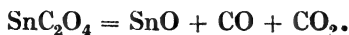
tend to accumulate and eventually cause serious injury to health. This is a most important fact in industry, as lead was formerly much used for glazing earthenware. Lead salts are also used in flint glass.

545. Tin occurs in nature as the oxide SnO_2 , as "cassiterite". Britain was known to the Phoenicians as the "Tin Islands", and Cornish tin is probably our oldest export. It is now found more abundantly in Malaya, in Uganda, and very abundantly in Bolivia. The oxide is easily reduced on heating with coal. The metal is soft and malleable. It has a crystalline structure and is incapable of bearing any considerable strain. At low temperatures it passes into an allotropic modification which tends to flake and pulverise. The metal is not much used pure except in tin-foil and in tin wire, which is used as an electrical fuse wire. The familiar tin ware is made of iron with a thin coating of tin to prevent rust. Tin is an ingredient of many important alloys, e.g. gun-metal (Cu 90 per cent., Sn 10 per cent.), bell metal (Cu 75 per cent., Sn 25 per cent.), speculum metal (Cu 67 per cent., Sn 33 per cent.), pewter (Pb 25 per cent., Sn 75 per cent.). All the proportions in these alloys are subject to slight variations, the alloys being mixtures, not compounds. Solder is an alloy of lead and tin of variable composition.

546. There are two series of tin salts, the **stannous salts**, in which the metal is *bivalent*, and **stannic salts**, in which it is *quadrivalent*. Stannous salts are normally produced when tin dissolves in a dilute acid, e.g.



Stannous chloride is a powerful reducing agent. **Stannous oxide**, SnO , is a black substance. It can conveniently be prepared by heating stannous oxalate, air being excluded:

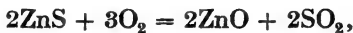


It is readily oxidised by air into stannic oxide, SnO_2 . This is a white compound insoluble in the usual acids and alkalis. The action of nitric acid on tin (§ 307) should here be recalled.

Stannic chloride, SnCl_4 , is remarkable as one of the few salts which are liquids under ordinary conditions. It is a fuming caustic substance and an oxidising agent.

547. Tin forms two sulphides, precipitated from solutions of stannous or stannic salts by H_2S . Obtained in this way stannous sulphide is very dark brown, stannic sulphide is yellow.

548. **Zinc**, another familiar metal, occurs in nature as the carbonate (ZnCO_3 , calamine) and the sulphide (ZnS , zinc blende). It is an easy metal to separate from its ores. The ores are roasted to give zinc oxide:



The oxide is then reduced with carbon—usually coal. As zinc boils at a little over 900°C . it is conveniently distilled over and allowed to solidify in moulds:



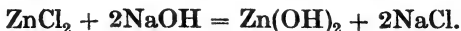
The appearance of zinc will be familiar, as it is used to form the outer coating of “galvanised” iron, the zinc being more permanent in air than iron and so protecting it from rust. The galvanising is effected by cleaning the iron and immersing it in molten zinc.

Zinc is used in a number of alloys (see § 536). Most of the more familiar kinds of electric battery contain zinc plates. The action of dilute acid on commercial zinc is already well known to the reader.

549. **Zinc oxide**, ZnO , is a white substance at ordinary temperatures, but when hot it is yellow. This fact is used in a test for zinc (see § 700). The oxide is quite regular in its properties, being soluble in dilute acids, and it can be prepared, as expected, by heating the hydroxide, carbonate or nitrate. It is commonly

prepared by heating the metal in air. Zinc oxide is used in ointments. It is also the basis of certain white paints. It has one advantage over lead in that it does not tarnish in presence of H_2S , lead sulphide being black whereas zinc sulphide is white.

Caustic soda precipitates zinc as a hydroxide, e.g.



The precipitate is soluble in excess of caustic soda. Zinc carbonate is a white powder precipitated by adding a solution of sodium bicarbonate to a solution of a zinc salt, e.g.

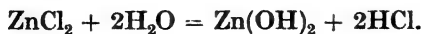


The use of Na_2CO_3 instead of NaHCO_3 gives a basic carbonate as in the case of copper (*q.v.*).

550. Zinc sulphide is a white substance not soluble in water but easily dissolved by even very weak acids. It is precipitated from a solution of a zinc salt by ammonium sulphide solution, thus:



551. The chloride, sulphate and nitrate of zinc are all white or colourless salts, easily soluble in water. The reader will have no difficulty at this stage in seeing how they may be prepared. One caution is, however, necessary. When zinc chloride is evaporated to dryness the residue is not ZnCl_2 , but a basic chloride, owing to a further action between the zinc chloride and the water, thus:



This is not complete, and the final residue is a compound of ZnCl_2 and Zn(OH)_2 —a basic chloride.

There are two ways of obtaining the dry chloride:

(1) By heating zinc in a stream of gaseous HCl .

(2) By mixing the solution of ZnCl_2 with excess of NH_4Cl .

On evaporating a double salt $\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$ remains as the

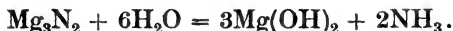
residue, and on heating strongly NH_4Cl is driven off and ZnCl_2 remains. Compare this with MgCl_2 (§ 197).

552. Magnesium is a metal something like zinc in its chemical properties. It is, however, far more difficult to extract from its compounds than is zinc. It can be prepared by heating magnesium chloride with sodium or—the more usual process now—by the electrolysis of fused magnesium chloride with calcium fluoride present as a flux. The pure metal is much used in ribbon form or as filings for flares, fireworks and flashlights. This is a matter of common knowledge. The metal, however, is justifying its place in this chapter as an industrial metal, as parts of aeroplane engines are now being made of magnesium. The metal is very light and in bulk is sufficiently permanent in air. If surprise be felt that such an apparently combustible substance as metallic magnesium can be put to such a use, it should be only necessary to remind the reader that even iron—the industrial metal *par excellence*—is itself easily oxidised and burnt when in a finely divided condition.

553. Magnesium will burn in nitrogen and is used to separate nitrogen from argon. Calcium can be used for the same purpose:



This nitride when treated with water yields ammonia:



Magnesium and zinc differ in one other important particular. Magnesium salts are commonly used in medicine, e.g. Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, whereas zinc salts are poisonous.

554. Aluminium is the familiar silvery white metal now so much in use in cooking utensils. Its introduction is modern. Thirty or forty years ago it was almost a curiosity. Yet, as it is a constituent of clay, it appears to be the most abundant metal in nature—more abundant even than iron. It is only comparatively recently that it has been possible to produce it cheaply.

It used to be made from AlCl_3 by heating it with sodium, but now it is produced from the oxide Al_2O_3 (e.g. bauxite) by electrolysis of a molten mixture of the oxide with cryolite, $\text{AlF}_3 \cdot 3\text{NaF}$. An important part of the process consists in purifying the oxide first.

555. Aluminium is a very valuable metal on account of its lightness. It is used in several important alloys. Magnalium is an alloy with 10 per cent. of magnesium. Aluminium bronze contains 10 per cent. of aluminium with 90 per cent. of copper. There are a large number of such alloys on the market, and research is continually adding to their number.

556. Aluminium oxide, Al_2O_3 , is a white and very insoluble powder. The hydroxide, $\text{Al}(\text{OH})_3$, is a flocculent precipitate which is formed when caustic soda solution is added to a solution of an aluminium salt. The precipitate is soluble in excess of caustic soda (cf. zinc hydroxide, § 549).

One of the most familiar salts of aluminium is alum, a double sulphate of aluminium and potassium: $\text{Al}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$. This is one of a class of salts, all called alums, even when no aluminium is present. They contain another trivalent atom (or radical) in place of the aluminium and a univalent one in place of the potassium. Thus chrome alum is $\text{Cr}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$, and ammonium alum is $\text{Al}_2(\text{NH}_4)_2 \cdot (\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$, and so on. They are discussed more fully in chap. xxxv.

A number of facts about aluminium have been incidentally referred to in the course of this book, and the reader will do well to go back and recollect them at this point.

557. Quite recently **beryllium** has commenced to take a place as an industrial metal. It is lighter than aluminium and nearly as light as magnesium, with a melting-point higher than either. Its future would seem to be assured if it can be found plentifully enough to be reasonably cheap.

Chapter XXXIV

IRON AND STEEL

558. **Iron** has for centuries been of first-rate importance to man. It is scarcely too much to say that the whole fabric of the material side of our present civilisation depends upon it. The extraction of iron from its ores and the production from it of steel and of alloys of iron of different kinds is a big technical subject demanding the whole-time consideration of the specialist. Here we can do no more than glance briefly at the main processes involved, cautioning the reader to remember that this is only the fringe of the subject, the actual operations being far more complicated. It is extremely helpful in studying a technical process to go over the works where the process is actually in operation, accompanied, of course, by a helpful and informative guide. A visit to an iron-works will throw much light on this chapter.

559. Iron is occasionally found native in nature, more particularly in masses of meteoric iron which fall upon the earth from outer space. The usual ores are oxides: **magnetite**, Fe_3O_4 , found largely in Scandinavia, and **haematite**, Fe_2O_3 , found in the north of England, in Spain and many other places abroad. A hydrated form known as **limonite** or **brown haematite**, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is fairly common, e.g. in South Wales. **Ferrous carbonate**, FeCO_3 , known as **spathic iron ore**, is found in many parts of England. It is common in an impure form, mixed with clay, as **clay ironstone** and **blackband iron ore**. About three-quarters of the steel of Germany used to be made from a brown haematite mined in Lorraine.

560. The main processes in the production of iron are not difficult to grasp. The ore is roasted to obtain dry Fe_2O_3 , which is a very infusible, reddish brown substance. This is mixed with

coke and limestone and the mass heated in a blast furnace, i.e. a furnace fed with a current of heated air. In this way the oxide is reduced to the metal, and the limestone at the same time forms a fusible mass or "slag" with the earthy impurities present, e.g. SiO_2 . The slag and molten iron produced in this way do not mix, the slag forming a separate layer on the top. A diagram of the usual form of blast furnace is seen in fig. 41. The iron and slag flow down to the receptacle at the bottom, iron being drawn off below, through the opening seen on the left. The slag is drawn off a little higher up. There are no other solid or liquid products. Fresh charges are added from time to time at the top and the furnace is kept at work for months on end. Both carbon and ferric oxide are very infusible and so cannot come into intimate contact. The reduction is effected by carbon monoxide, generated by the oxygen of the air in presence of an ample supply of hot carbon and also by the action of the heat on the mixture

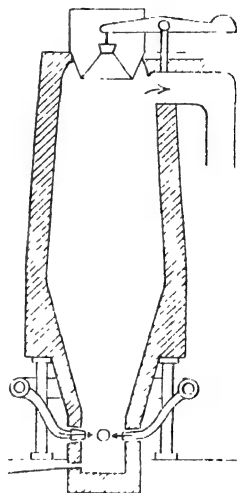


Fig. 41. Blast furnace.

of limestone and carbon (see § 242). The carbon dioxide formed in this process is continually being reduced to CO by the coke, and it is largely CO which passes off at the top. This being combustible it is used as a fuel to heat the air used in the blast. The iron produced—cast iron—in this way is run into moulds and in this moulded form is known as "pig iron". It usually contains a fair amount of carbon, up to a maximum of nearly 5 per cent. The metal is purified by "puddling". In this process the iron is heated with ferric oxide with access of air. The

molten mass is kept stirred, when most of the carbon, together with such other impurities as sulphur, is thus eliminated and a much purer form of iron is produced. At this stage the iron is subjected to a great deal of mechanical treatment—rolling and hammering—the final product being the purest of the common forms of commercial iron, known as “wrought iron”. Wrought iron contains less than 0·2 per cent. of carbon. Pig iron is brittle. Wrought iron is very tough and malleable and has a higher melting-point than cast iron.

561. Steel. These two forms of iron, pig iron or cast iron, and wrought iron, are the starting-points of a number of specialised forms of iron, the chief of which is steel. Steel is a special kind of iron containing an amount of carbon varying from 0·3 to about 1·5 per cent., according to the hardness of the steel required—the greater the carbon content the greater the hardness. It normally contains less carbon than cast iron and more than wrought iron, and the method of production therefore varies according to the raw material from which it is made.

562. A very hard form of tool steel is produced by packing the purest wrought iron in infusible fire-clay boxes with charcoal. The whole is then heated until the iron softens, i.e. up to about 1000° C., and the heating is continued for over a week. At the end of that time the iron is found to have absorbed a quantity of the carbon. The mass is then melted and subjected to rolling and hammering to secure uniformity of texture and in this way a high-class steel can be produced. The slowness of the process is a practical disadvantage. This method is termed the **cementation process**.

563. In the **Bessemer process** the steel is produced from cast iron, run straight from the blast furnace into the “Bessemer converter”, a large oval-shaped container, capable of being revolved by machinery about a horizontal axis (see fig. 42). The converter is lined with a very infusible sandstone. A strong current of air is passed in under high pressure at the base. This burns away

the carbon, the heat of combustion serving to keep the charge molten. During this stage the metal is converted into nearly pure iron. The requisite quantity of carbon is then added. In practice the actual substance introduced contains iron, manganese and carbon and is called "spiegeleisen". The blast of air mixes the materials, and the steel is soon ready to be cast into moulds.

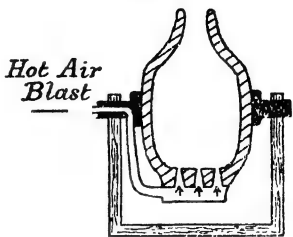


Fig. 42. Bessemer converter.

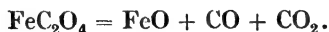
The presence of sulphur in steel causes it to be brittle when hot, or "hot short"; phosphorus makes it brittle even when cold, i.e. "cold short". Both these impurities are very undesirable, especially phosphorus. If they are present the Bessemer converter is lined with a mixture of the oxides of calcium and magnesium, instead of sandstone. In this way the sulphur and phosphorus are converted into sulphates and phosphates. The phosphates so produced are useful as fertilisers and this "basic slag", a waste product of the Bessemer process, is put on the market as a manure. The Bessemer process takes under half an hour and so is very strikingly quicker than the cementation process.

564. The most usual process now is the **Siemens-Martin process**. It differs but little in chemical principles from the Bessemer process, though in the mechanical details it differs considerably. It is worked, however, in an open hearth, the air being pre-heated to secure higher and more uniform temperatures. The main advantage of the process is that it is slower than the Bessemer process, without being too slow. It takes about eight hours. At this speed the different stages of the process are under better control and they can be watched and modified more accurately. It is the most extensively used modern method.

Various types of steel are manufactured containing different

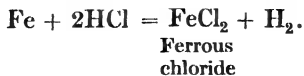
566. Compounds of iron. Iron forms two series of salts, the **ferrous** salts, in which it is *bivalent*, and the **ferric** salts, in which it is *tervalent*. Ferrous salts when hydrated or in solution are usually very pale green, ferric salts being, under these conditions, reddish brown, yellow or red.

Ferrous oxide is produced as a black powder by heating ferrous oxalate in absence of air:



It readily burns in air to Fe_2O_3 . With dilute acid it yields ferrous salts.

When iron dissolves in a dilute acid it is the ferrous salt which is produced, e.g.



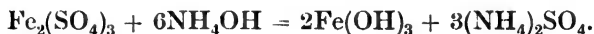
The action of strong nitric acid upon iron has already been described. The reader should turn back, also, to the reference to

ferrous sulphate (§ 353) and to the production of magnetic oxide of iron (§ 34).

567. Ferrous sulphide, FeS , is a black substance easily produced by heating an intimate mixture of the right quantities of iron filings and sulphur. Iron disulphide, FeS_2 , is the mineral iron pyrites. This has a brassy appearance and has even been mistaken for gold.

568. Ferric oxide, Fe_2O_3 , already referred to as a mineral, can be prepared by heating ferrous sulphate (see § 353). It is a very hard powder and is useful for polishing. Fe_2O_3 dissolves in dilute acids yielding ferric salts, but some forms of the oxide, notably after considerable heating, can only be dissolved with extreme difficulty.

569. Ferric hydroxide, $\text{Fe}(\text{OH})_3$, is precipitated as a brown flocculent precipitate when an alkali is added in solution to a ferric salt, e.g.



The hydroxide is soluble in a concentrated solution of ferric chloride. On heating it gives up water and ferric oxide remains.

570. Ferric salts are obtained when ferric oxide or ferric hydroxide is dissolved in acids. When dry chlorine is passed over heated iron, anhydrous ferric chloride is formed. From this ferric hydroxide can be prepared as above, and this, on dissolving in dilute H_2SO_4 , gives ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$. Both ferric sulphate and ferric chloride are acid in solution. The reader should have no difficulty at this stage in explaining this (see § 458). Ferric sulphate forms alums (see § 556). For example, ferric ammonium alum has the formula $\text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$. There is no ferric carbonate known, but ferrous carbonate has been referred to as the mineral ore, spathic iron. This carbonate is precipitated in a basic form (cf. copper) when a ferrous salt and sodium carbonate are mixed in solution. A ferric salt mixed

with sodium carbonate solution would yield ferric hydroxide and carbon dioxide. It is a useful exercise to compare ferric salts with aluminium salts.

571. Two further matters of interest may be mentioned about iron before we leave it. In the first place iron is one of the great colouring materials of nature (see § 402). The bright colours of rocks are nearly always due to iron, and iron serves the mineral world in this way as the totally different substance chlorophyll serves the vegetable world. Iron compounds are used, too, in the arts as pigments; rouge, red ochre and yellow ochre, for example, are all preparations of ferric oxide.

572. In the second place iron is of the greatest importance because of its magnetic properties. Soft iron is readily magnetised, but will not retain its magnetism. Hence it is useful for the cores of electromagnets and has been much used in electromagnetic machinery. Ordinary steel, on the other hand, will retain its magnetism and is invaluable for permanent magnets, including compass needles. In this way iron makes a further and very remarkable contribution to the world's work. Manganese steel containing 12–16 per cent. of manganese is, however, not magnetic. Silicon steel, containing 4 per cent. of silicon, is used extensively in making electromagnets and transformers, as it can readily be magnetised and demagnetised.

Chapter XXXV

ISOMORPHISM

573. When a substance passes from a liquid to a solid state (as, for example, when molten sulphur cools or when a salt solution is evaporated to beyond the saturation point), the resulting solid frequently—though by no means always—appears in a crystalline form. As a general rule, the more slowly the crystals are formed the larger they will be. If a solution of a salt is allowed to crystallise by the slow process of evaporation at ordinary temperatures, bigger and better crystals are produced than if the solution is rapidly evaporated by heating.

574. A complete crystal has a definite geometrical shape. It is not our purpose here to go into the details of crystal forms. It may be noted, however, that crystals can be regarded as built

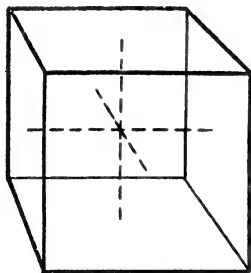


Fig. 43. Cube.

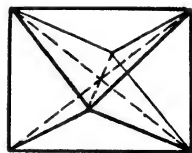


Fig. 44. Octahedron.

up around certain axes, and there are six different crystal systems, classified by means of the relative sizes of these axes and the angles between them. For example, the simplest is the “regular” system. Crystals belonging to this system are built up around three equal axes, all at right angles, and this leads to two

different geometrical shapes, the cube and the octahedron (see figs. 43 and 44, in which the three axes are dotted in).

575. Besides the outside crystal shape, the material of the crystal has itself a definite internal structure, so that a crystal can be recognised and its properties examined if only broken and irregular bits of the crystal are available. Most of this, however, is work involving a somewhat advanced knowledge of the theory of light, the examination being made with a microscope.

576. Now let us turn to the question of the formation of crystals from a solution of mixed salts. We will begin with the case in which two salts are present and consider as an example one which should now be familiar, the solution of KCl and KClO_3 formed by passing chlorine through a hot solution of KOH (see § 209). If this is evaporated the first crop of crystals consists of KClO_3 , since this salt is at lower temperatures by far the less soluble of the two. There comes a stage, however, as the evaporation proceeds, when the saturation point is reached for *both* the salts. What happens then? Do we get crystals of mixed composition? In this case we do not. When the KCl starts to crystallise, crystals of both salts appear side by side mixed together, but *each crystal is a separate body and contains one or other of the two salts but not both.*

577. Exactly what happens when a crystal is in process of construction from a solution is beyond our ken. But obviously the controlling power, whatever may be its nature, is unable to fit a molecule of KCl into a growing crystal of KClO_3 ; it would be like putting the proverbial square peg into a round hole.

If we had a heap of flat pieces of wood of the same thickness, some of them square and some of them hexagonal, all the edges being equal, it would be easy to make out two pieces of tessellated pavement, using for one the square pieces and for the other the hexagonal. It would clearly be a much more difficult matter to work pieces of both types into one pattern. There must be some innate difference between the ultimate particles of KCl and

KClO_3 which makes them incapable of being built up into the same crystal. So crystallisation yields crystals of two separate kinds.

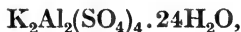
578. But it might conceivably be possible to find two different salts whose structures were so much alike that for the purpose of building up a crystal a molecule of the one would serve as well as a molecule of the other. Cases of substances whose molecules can replace each other indifferently in crystals are quite common, and experience shows that this power of replacement is usually an indication of close similarity of chemical constitution. Such substances are said to be **isomorphous**, and if two substances are to be regarded as isomorphous they must obey the following three laws:

(a) they must crystallise in the same crystalline system;

(b) a crystal of one of the substances placed in a saturated solution of the other will continue to grow, acquiring a layer of the second;

(c) from a mixed solution of the two substances mixed crystals can be found containing the two substances in any proportions.

This last statement must be modified in one important particular, namely, that the proportions of the two substances must depend upon their relative solubilities. For example, potassium alum,



and rubidium alum, $\text{Rb}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$,

are isomorphous, but the former is by far the more soluble. Hence if a solution of these two salts mixed in about equal proportions be evaporated, the first crop of crystals will be rubidium alum, since it will be deposited when the solution is saturated with respect to this salt, at which stage it is not nearly saturated with respect to the potassium salt. The mixed crystals will be deposited at a later stage when the concentration of the potassium alum has reached saturation, and by then most of the

rubidium alum will have crystallised out. At this point mixed crystals will appear, each crystal containing molecules of both alums. Their composition can be varied by varying the temperature at which the evaporation is taking place, since the solubilities of the salts vary differently with the temperature. Thus the proportions of the two salts present in such a mixed crystal are severely limited by their relative solubilities. It would clearly not be possible to make mixed crystals containing a large excess of the less soluble ingredient. The point to mark carefully, however, is that such mixed crystals do not contain the two salts in fixed molecular proportions, as would be the case were the two salts in the crystal chemically combined, and also that the actual proportions present depend upon a physical property—solubility—and not upon the respective molecular weights, a chemical property. Hence it is clear that we are here dealing with an intimate mixture, not a chemical compound.

It may be noticed that, for the purpose of defining isomorphism, law (*a*) is logically unnecessary. It will never happen that substances obey laws (*b*) and (*c*) without obeying law (*a*), and obedience to laws (*b*) and (*c*) would be sufficient proof that the substances obeyed law (*a*), i.e. that their crystals belonged to the same system.

579. Isomorphism, then, is usually decisive evidence of a strong similarity in chemical structure. Thus, to keep to the example of the alums, the most famous group of isomorphous salts, the formula of all the alums may be written



where *M* stands for a univalent (i.e. monovalent) metal, and *T* for a tervalent metal. *M* is commonly K, Na or—and this point is very interesting—NH₄ (see § 278). Rarer alums contain rubidium, thallium or silver as the monovalent metal or radical. *T* is usually aluminium, chromium or ferric iron. Certain rare tervalent elements may also occur in this position. The sulphur

may be replaced by selenium, the oxygen and the water being the only invariable parts of the molecule.

580. The formulae of two isomorphous substances in general agree exactly in the way the formulae of two different alums agree. They agree atom for atom, the only difference as we pass from one to another being the change from one atom or radical to another, always and of necessity of the same valency.

581. It will be easily seen that the principle of isomorphism may be used in some cases to settle an atomic weight. For example, the formula of chrome alum is



Now potash alum (whose percentage composition can be determined practically) is isomorphous with this, and, without any previous knowledge about the valency or the atomic weight of aluminium, we can deduce by the principle of isomorphism that aluminium is trivalent and that the formula of potash alum is



Note that the water of crystallisation is an important item in such formulae. Only molecules containing the same number of molecules of water of crystallisation can yield isomorphous crystals. Directly we know this formula, the atomic weight of aluminium is easily settled. There are, for example, as many atoms of aluminium as of potassium. The atomic weight of potassium is 39, and if the atomic weight of aluminium is x , x gm. of aluminium are clearly present for every 39 gm. of potassium. So that once the percentage composition of the salt is determined, the determination of x is merely to answer the question: How many grammes of aluminium are present for every 39 gm. of potassium? If the reader examines this carefully, he will see that x is also the number of grammes of aluminium present to every 192 gm. of the SO_4 group. Thus the question of the atomic weight of aluminium could be approached from this point.

582. The atomic weight of aluminium can be more conveniently found from the following considerations. Ammonium aluminium sulphate satisfies all the tests for isomorphism with the other alums, and so must itself be an alum. Hence its formula is



and aluminium must be trivalent, so its oxide will have the formula Al_2O_3 .

Now when ammonium alum is heated it decomposes and leaves aluminium oxide as a residuc. If then a weighed amount of the alum be heated until it ceases to lose weight on further heating, we clearly have, x being the atomic weight of aluminium:

$$\frac{\text{weight of the alum taken}}{\text{weight of residuc}} = \frac{2x + 852}{2x + 48},$$

from which x can easily be calculated. This is a very trustworthy method of finding the atomic weight of aluminium.

583. The alums provide such a striking case of isomorphism that every text-book uses them as an example of it. Indeed, the study of isomorphism is occasionally introduced almost as if it were a side issue in the study of alums. It is well, therefore, to remember that isomorphism is a common phenomenon. Chlorides, bromides and iodides of the same metal are usually isomorphous, so also are most zinc salts with the corresponding magnesium and ferrous salts. Potassium perchlorate, KClO_4 , and potassium permanganate, KMnO_4 , are isomorphous, and so on. A series of naturally occurring carbonates, CaCO_3 , MgCO_3 , FeCO_3 , ZnCO_3 and MnCO_3 , is known of which the members are isomorphous.

584. Earlier in the chapter an analogy was drawn between the fitting together of squares and hexagons and the fitting together of the molecules to form a crystal. This analogy must not be pressed too far. The structure of crystals is a more complicated question than such a simple picture suggests. One may

be pardoned for being puzzled at finding that the substitution of a comparatively complicated group like NH_4 or of an atom of silver for an atom of sodium leaves the shape unchanged. The reader may reflect on this at his leisure. What is, however, abundantly clear and the thing that matters is this: that isomorphism is normally an indication of close similarity of chemical constitution, and this is exhibited by the formulae in the way we have described.

The student who is interested in this subject and wishes for further information should read Bragg's *X-rays and Crystal Structure*.

PART II

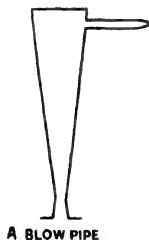
Chapter XXXVI

APPARATUS AND MANIPULATIONS

585. The following are a few hints on the apparatus and simpler methods employed in the laboratory; attention to them will be amply repaid by success in experimental work. Good results cannot be obtained unless care is taken in fitting up the apparatus and in such simple operations as bending glass tubing, boring corks and adjusting filter papers. Success in quantitative experiments can only be attained by careful weighing.

APPARATUS

586. The source of heat. The Bunsen burner. If the tube of a Bunsen burner is unscrewed, a small jet will be seen. If the gas is lighted at this jet, a long ordinary gas flame is produced. When the burner is used in the ordinary way, the gas issuing from this jet draws air in through the holes at the side of the tube.



A BLOW PIPE

Fig. 45.

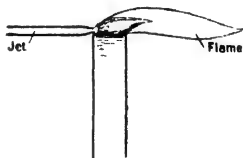


Fig. 46.

This mixture of air and gas burns at the top of the tube in a non-luminous and hot flame.

Blowpipe flame. By using a mouth blowpipe (figs. 45 and 46)

and a Bunsen flame, a hotter flame can be directed on a substance to be heated. The device in fig. 39 can be used.

587. A water bath consists of a pan (such as a metal saucepan) on the top of which can be placed a basin containing a liquid which is to be evaporated or a flask of liquid which is to be heated to 100°C . The bath is frequently provided with a set of metal rings, which enable the opening to be varied in size.

A desiccator (fig. 47) is a glass vessel fitted with an air-tight lid; it is used for keeping apparatus or material which must be prevented from absorbing moisture.

The apparatus or material (on a watch-glass or basin) is placed on a perforated metal tray which extends across the middle of the desiccator.

The lower part contains calcium chloride or concentrated sulphuric acid, either of which will absorb moisture and dry the air in the desiccator.



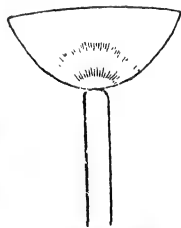
Fig. 47. Desiccator.

MANIPULATIONS

588. Cutting, bending, and blowing glass tubing. To cut narrow glass tubing, draw a sharp triangular file or a glass knife quickly across the tube until a notch is made. Hold the tube in both hands, with the notch downwards and the thumbs meeting just above the notch. Press the thumbs downwards, when the tube will break.

Wider glass tubing can be cut by making a notch all round the tube and then touching one point of the notch with the red-hot end of a piece of fine glass rod.

To bend glass tubing, use a fish-tail burner (luminous flame) (see fig. 48). Hold the tube in both hands, one on either side of the flame, and rotate the tube



4. FISH TAIL FLAME

Fig. 48.

steadily. When the glass has been softened, bend the tube somewhat slowly, either in the flame or outside it. In many cases this can be conveniently done by supporting one end of the tube with the finger, which is slowly lowered until the required curve is made. Do not hurry the bending, otherwise a kink will be made which will easily break.

To **draw** out glass tubing, the tube must first be softened by rotating it in the Bunsen flame or in the blowpipe, supporting it with both hands, one on either side of the flame. Allow the glass to collapse and thicken; remove the tube from the flame and draw the hands apart (see fig. 49 *A*).

To **seal** a tube and **blow** a bulb. Draw out the tube as at *A*; turn the blowpipe down to a fine jet and heat the tube just where it begins to narrow; when the glass is soft draw the hands quickly apart. The tube is now sealed. It will be well to soften the end in the blowpipe and then blow down the open end to produce the effect shown in *B*.

To blow a bulb on a tube, first seal it up, continue heating it and rotating it until a small quantity of molten glass is formed. Remove the tube from the flame and blow down the open end to form a bulb as at *C*. If a larger bulb is required, the heating must be repeated until a sufficient quantity of molten glass has been obtained to enable a larger bulb to be blown (see *D* and *E*). The walls of the bulb should be of uniform thickness.

589. To bore a hole in a cork. Select a cork slightly larger than is required to fit the flask or tube. Soften it by

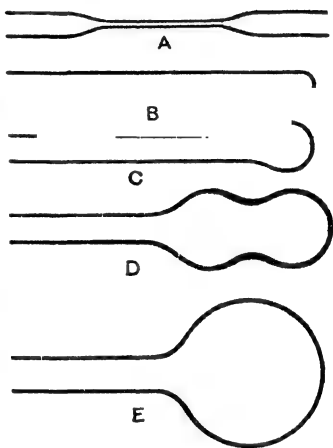


Fig. 49. Drawing glass tubing.
Blowing a bulb.

rolling it gently under the foot. Select a borer slightly smaller than the tubing which is to pass through the cork. Wet the borer and press it steadily into the narrower end of the cork, rotating the borer all the time. Wet the tubing before working it into the hole in the cork; hold the cork and tubing as shown in fig. 50.



Fig. 50. Inserting tubing into a cork.

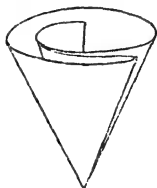


Fig. 51. Folding a filter paper.

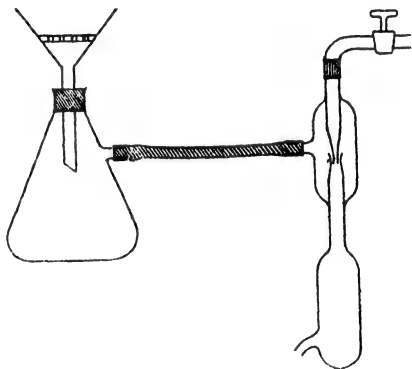


Fig. 52. Rapid filtration.

590. Filtering. Fold a circular filter paper across the centre to form a half circle and then again to form a quadrant. Then take three thicknesses of the paper and press inwards with the finger to form a cone (see fig. 51). Fit the paper inside the filter funnel, wet the paper and adjust it so that the paper touches the glass; this may require a little care.

For rapid filtration fit the funnel into a cork in a filter flask and attach the side tube to a vacuum pump (fig. 52). Place in the funnel a perforated porcelain plate and fit an unfolded filter paper over the plate. When you have finished filtering, detach the flask from the pump before you turn off the water.

591. Using a balance. Observe the following rules:

(1) See that the weights are correct before and after use and that they are in their correct places in the box.

(2) Never put anything into or remove anything from either pan while the balance is swinging. Never leave it swinging.

(3) Before beginning to weigh see that the balance is correctly adjusted.

(4) Place the substance to be weighed in the left-hand pan. Raise the lever gently and only turn it completely over when a balance is nearly obtained.

(5) Do not touch the weights with your fingers.

(6) Never weigh anything hot; take care that the outside of any vessel which is to be weighed is dry.

(7) Count the weights both by the number on the pan and by the vacant spaces in the box.

592. Entering notes on observations and results. Notes should be entered as near as possible to the time of observation. It is best to enter them direct into a neat note-book; they should never be recorded on odd pieces of paper. It is inadvisable to use a rough note-book. Entries of numerical results should each occupy a single line, the particular unit of measurement (gm., c.c., etc.) should be stated. In many instances the difference of two measurements is required; it is best to put the greater above the smaller, even if the greater measurement is obtained after the smaller one. In such instances, record both measurements in your note-book and not merely the difference.

Chapter XXXVII

ELEMENTARY EXPERIMENTS

MIXTURES AND COMPOUNDS

593. The difference between mixtures and compounds is explained in chap. I, §§ 9 and 10. The following experiments illustrate some of the principal differences.

EXPERIMENT 1. Separation of a soluble from an insoluble substance. (A mixture of sand and potassium nitrate will be suitable.)

Take about half a test-tube full of the mixture, place it in a beaker and cover it with about 50 c.c. of water. Warm the liquid (on a tripod and gauze) with a Bunsen burner, stirring with a glass rod. After about 10 min. pour the liquid down the glass rod into a filter paper in a funnel and receive the clear liquid in a porcelain basin. Wash the residue in the beaker into the funnel by means of a jet of water from a wash bottle (see fig. 53). Wash the solid on the filter paper with distilled water and collect the washings as before.

Evaporate the liquid in the basin with care, first of all over a Bunsen flame; as soon as there is any sign of spurting, finish the evaporation on a water bath.

Dry the filter paper in the funnel by heating it in a steam oven or air oven at 105° C.).

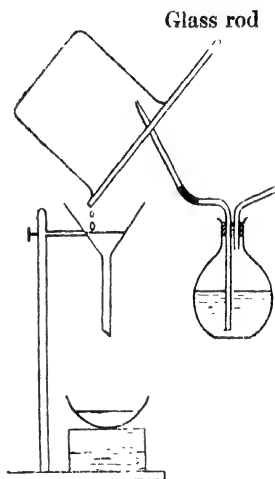


Fig. 53. Separation of a soluble from an insoluble substance.

The mixture has thus been separated into its two constituents by making use of the fact that one of the constituents is soluble in water but the other is not.

EXPERIMENT 2. Difference between a mixture and a compound.

Examine some iron filings and observe that they are attracted by a magnet. Place a small quantity in a test-tube and add some dilute hydrochloric acid and warm. Observe what happens.

Examine some flowers of sulphur (or powdered sulphur) in the same way.

Weigh out about 7 gm. of iron filings and 4 gm. of sulphur; mix them thoroughly on a sheet of paper. Examine small portions of this mixture with a lens, a magnet and some dilute hydrochloric acid. Can you detect each of the constituents?

Pour the remainder of the mixture into a dry test-tube and press it firmly down. Holding the test-tube in a test-tube holder, heat the bottom of it with a Bunsen flame. As soon as the reaction begins, remove the flame. When the reaction has finished, dip the hot tube into cold water in a basin; the end will crack and the solid can be separated from the glass.

Examine this solid with a lens and with a magnet. Place a *small* portion in a test-tube and add some dilute hydrochloric acid; do not hold the test-tube close to your nose. As soon as you have made your observations, pour the liquid into the sink and flush well with water.

You have thus sufficient evidence to decide whether the substance formed by heating iron and sulphur together has any of the properties of a mixture of iron and sulphur.

SOLUBILITY

594. Change of solubility with temperature (see § 91).

EXPERIMENT 3. A wide boiling tube *A* is fitted with a cork, thermometer *T* and stirrer *S* (see fig. 54). It is supported in a

beaker *B* containing water, in which is a thermometer *V* and stirrer *P*.

20 c.c. of distilled water are placed in *A*; the water in *B* is heated to 25° C. Add to *A* 2.5 gm. of potash alum and stir; this will all dissolve. Add a further 1.5 gm. and stir again for 10–15 min. The whole of the alum will not dissolve and the solution is therefore saturated.

Raise the temperature in *B* to 40° C. and stir both liquids. The alum in *A* will quickly dissolve; add 2 more grammes of it and stir again. Some will remain undissolved.

Raise the temperature to 60° C.; the alum will dissolve. Add 7 more grammes of it and stir again. Some will remain undissolved.

Raise the temperature to 80° C.; the alum will dissolve. Add more alum in 1 gm. lots one after another, pausing (but stirring) after each addition to see whether what has been added will dissolve and stopping the additions when it is certain that the solution is saturated.

In this way a rough idea of the solubility of alum at 25°, 40°, 60° and 80° C. can be gained. When the solution is saturated at 80° C., withdraw the tube *A* and cool it in running water, when much of the dissolved alum will separate from solution.

EXPERIMENT 4. Solubility of a solid (potassium nitrate) in water at 25°, 40° and 60° C. (see § 95).

The method which is described below will give results of satisfactory accuracy. Results of greater accuracy can be attained by using a special apparatus (called a thermostat) for maintaining the liquid at the proper temperature and by using a mechanically operated stirrer.

Support a 250 c.c. beaker *A* (fig. 55 *a*) in a water bath *B* by covering the water bath with a piece of metal sheet in which a

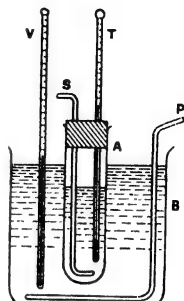


Fig. 54. Determination of solubility.

hole has been cut just large enough to admit the beaker but not large enough to allow it to slip through. A stirrer *S* (preferably of glass) and a thermometer *T* are required in the beaker, and another thermometer *V* and stirrer *P* in the water bath.

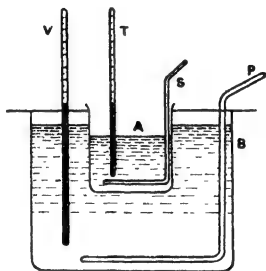


Fig. 55 a. Solubility apparatus.



Fig. 55 b. Pipette with filter.

Fit a dry 20 c.c. pipette with two pieces of rubber tubing (see fig. 55 b). The tubing at the top of the pipette is closed with a clip *E*; to that at the bottom is attached a small piece of glass tubing *G* drawn out to a jet and filled with glass-wool to serve as a filter.

Place in the beaker 150 c.c. of water, 45 gm. of potassium nitrate, raise the temperature of the bath to 25° C. and keep it at that temperature as exactly as you can.

Stir both the water in the bath and the liquid in the beaker continuously for 15 min. Allow the solution to settle for 5 min., keeping the temperature constant at 25° C.

Weigh a weighing bottle. By means of the pipette above described withdraw a quantity of the saturated solution; remove the filter from the end of the pipette and allow the liquid to run into the weighing bottle; close the bottle and weigh it.

Pour the contents of the weighing bottle into a weighed

evaporating basin; wash the inside of the bottle by means of a jet of distilled water, allowing the washings to run into the evaporating basin. Evaporate the solution to dryness on a water bath, and when dry transfer the basin to an air oven heated to 130°C . Keep the basin at this temperature for half an hour, cool it in a desiccator and re-weigh. Heat the basin in the oven for a further 10 min. and weigh again. Repeat the heating until the weight is constant.

Stir the solution in *A* for a further 10 min. at 25°C ., withdraw another portion of solution and find its composition as before. If the two analyses agree, the solubility may be calculated. Record your results as follows:

Temperature 25°C .

Weight of bottle and solution =

Weight of bottle =

Weight of solution =(*S*) gm.

Weight of basin and solid =

Weight of basin =

Weight of solid =(*M*) gm.

M gm. of solid were dissolved by $S - M$ gm. of water; hence calculate the weight of solid which would be dissolved by 100 gm. of water.

Now raise the temperature of *B* to 40°C . and determine the solubility at that temperature. If the solid should all dissolve, add some more; and if the amount of water should appear too small add some more, but take care to stir the liquid for 15 min. after the addition of more water. A dry pipette with a clean dry filter must be used for each determination. It will be best to warm the pipette before use to prevent any solid crystallising in it.

After the solubility at 40°C . has been determined, raise the temperature to 60°C . and make a determination at that temperature.

LOSS OF WEIGHT

595. Water of crystallisation. Many salts which crystallise from solution in water are compounds of the salt with water; the two are combined in absolutely definite proportions and constitute a compound and not a mixture (see § 92).

EXPERIMENT 5. That the compounds contain combined water may be shown by heating them in test-tubes and condensing the water which is driven off in a cooled test-tube as in fig. 56. The crystals shown there are of alum; other suitable salts are copper sulphate (blue vitriol), magnesium sulphate (Epsom salts), sodium carbonate (washing soda), sodium sulphate.

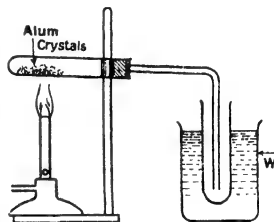


Fig. 56. Water of crystallisation.

596. Determination of the percentage of water of crystallisation.

EXPERIMENT 6. The determination of the percentage of water of crystallisation is a useful exercise.

Heat a clean porcelain crucible on a pipe-clay triangle over a Bunsen flame and allow it to cool in a desiccator (fig. 47). Weigh it accurately.

Powder some crystals of barium chloride in a mortar and leave the powder on a pad of filter paper overnight in a dry cupboard (not in a desiccator).

Place about 2 gm. of the powder in the crucible and weigh accurately.

Heat the crucible and contents gently for 15 min.; allow to cool in a desiccator and re-weigh. Heat, cool and weigh again. Repeat the heating and cooling until the weight is constant.

Record your results as follows:

Weight of crucible and crystals	=
Weight of crucible	=
Weight of crystals	=(<i>H</i>) gm.
Weight of crucible and residue	=
Weight of crucible	=
Weight of residue	=(<i>S</i>) gm.

H gm. of crystals have been found to contain *H* - *S* gm. of water of crystallisation; hence calculate the weight of water contained in 100 gm. of crystals.

Other suitable salts are potash alum, washing soda (choose clear crystals) and sodium sulphate.

597. Determination of the percentage loss of weight of a carbonate on heating.

EXPERIMENT 7. Heat a clean porcelain crucible on a pipe-clay triangle over a Bunsen flame. Allow to cool in a desiccator and weigh accurately.

Place in the crucible about 2 gm. of the powdered carbonate and weigh accurately.

Heat the crucible and contents at first gently and then strongly. Allow to cool in a desiccator. Re-weigh. Heat, cool and weigh again. Repeat until the weight is constant.

Record the results and calculate the percentage loss of weight as described in Exp. 6.

Chapter XXXVIII

THE PREPARATION AND COLLECTION OF GASES

598. The preparation of the common gases does not as a rule present any particular difficulty. The apparatus required is very simple and not expensive, especially if small flasks and small gas jars are employed. A flask of 250 c.c. capacity will be large enough and in many instances flasks of 50 c.c. capacity will suffice; or boiling tubes about 5 in. by $\frac{3}{4}$ in. can be used. Jars of about 50 c.c. capacity will contain sufficient gas for most tests and in only a few instances need larger jars (say 150 or 300 c.c.) be employed. If small apparatus is used, less quantities of reagents are required and less time is needed.

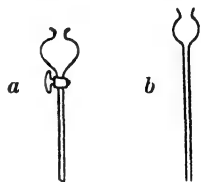


Fig. 57. a. A tap funnel.
b. A thistle funnel.

The secret of success in collecting gases is to make sure *that the apparatus does not leak*. Corks should fit tightly in flasks or test-tubes and the holes should be bored so that the tubing which passes through them fits closely. Attention to these details will save much time.

In order to introduce liquids into the flask or tube after the apparatus has been set up a tap funnel (fig. 57, a) or a thistle funnel (fig. 57, b) is used. Tap funnels are best but are somewhat expensive; a thistle funnel *must* be pushed so far through the cork that the lower end is covered by liquid. An ordinary funnel connected to a straight piece of glass tubing by a rubber tube and clip forms a fairly efficient substitute for a tap funnel.

Gases are frequently collected over water; for this purpose a glass or earthenware trough is required. The gas jar stands on a

beehive shelf under which the delivery tube passes (figs. 58 and 59).

A **deflagrating spoon** is used for burning substances like sulphur or carbon in jars of gas. It consists of a small metal cup attached to a wire which passes through a cork in a circular metal plate (fig. 9).

Chapter XXXIX

OXYGEN

599. EXPERIMENT 8. Preparation from sodium peroxide and water.

This is the easiest method. The apparatus shown in fig. 58 or fig. 59 can be used. For that shown in fig. 58 about 6 gm. of sodium peroxide are placed in the tube and water is run in a little at a time through the funnel; from this 800 c.c. of oxygen can easily be collected.

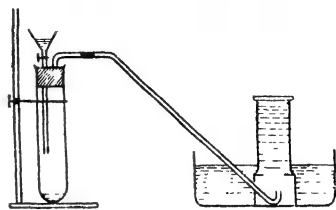


Fig. 58. Preparation of Oxygen.

For that shown in fig. 59 about 10 gm. of sodium peroxide are placed in the flask, and water in the tap funnel. A few drops of water are run in; oxygen is rapidly evolved and is collected in the gas jars. Collect four jars of about 50 c.c. and one jar of 500 c.c. capacity and also a test-tube of it which you can cork up.

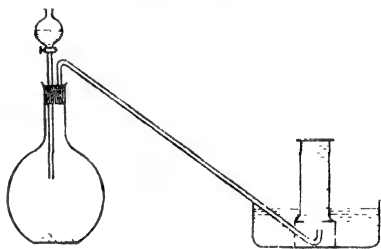


Fig. 59. Preparation of Oxygen.

Properties of oxygen.

(a) Put into one jar a glowing splinter of cedar wood. The splinter will burst into flame. Oxygen and nitrous oxide are the only gases which have this property; you will be told in § 670 how to distinguish between them.

(b) Put some sulphur into a deflagrating spoon (fig. 9). Heat it in a Bunsen flame till the sulphur catches fire; put the spoon into a jar of oxygen. Note what happens when the sulphur has

ceased burning. Cautiously smell the gas; it is sulphur dioxide, SO_2 . Add a little water; replace the plate and shake well. Add blue litmus to the remaining solution; you will see that a substance has been produced which turns litmus red.

(c) Repeat with a little piece of phosphorus (*take care not to touch phosphorus with your fingers*). Again note what happens. When the phosphorus ceases burning, remove the spoon and cover the jar with a greased plate. Heat the spoon in a flame until all the phosphorus has burnt away. Add a little water to the jar, replace the plate and shake well. The fumes dissolve. Add litmus; you will see that another substance has been produced which turns litmus red.

(d) Repeat with charcoal, heating the charcoal red hot before plunging it into the jar of oxygen.

The gas produced is called carbon dioxide, CO_2 .

Substances which turn litmus red are acids. You will now see why this gas is called the "acid producer" or "oxygen".

(e) Again take a spoon and attach to it some pieces of magnesium ribbon. Light the ribbon in a flame and plunge it into a jar of oxygen. Note what happens. Shake up the white powder with hot water and add a few drops of phenolphthalein. The pink colour will show that an alkali has been produced—not an acid this time.

(f) Now take the larger jar, and put a little sand into it. Fasten a bundle of fine iron wires to a spoon, heat their ends in a flame and dip them into a little sulphur. The sulphur will catch fire. Plunge the wires at once into the jar of oxygen. The iron wires will burn readily.

(g) Take the test-tube full of oxygen. Pour in about 5 c.c. of caustic soda solution and add quickly 2 gm. (or a teaspoonful) of pyrogallol (pyrogallous acid). Cork up tightly and shake.

Take out the cork under water (fig. 60). The pyrogallol solution

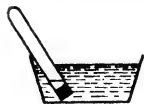


Fig. 60. Absorbing Oxygen.

has turned brown and dissolved the oxygen. This reaction may be used for detecting oxygen in a mixture of gases such as air and for determining the percentage (by volume) of oxygen in such a mixture.

600. Other methods of preparation. Oxygen can also be prepared by the action of heat on either (a) potassium chlorate, or (b) mercuric oxide.

EXPERIMENT 9. From potassium chlorate. For this purpose the apparatus shown in fig. 61 is required.

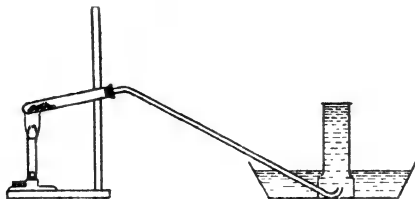


Fig. 61. Preparation of Oxygen from Potassium Chlorate.

A hard glass test-tube about 13 cm. long and 15 mm. bore is required; 450 c.c. of oxygen can be collected from 2 gm. of potassium chlorate.

Oxygen can be prepared more easily from potassium chlorate if the latter is mixed with manganese dioxide. That this is so can be shown in the following way.

EXPERIMENT 10. From potassium chlorate and manganese dioxide. Heat about 6 gm. of dry potassium chlorate (alone) in a hard glass test-tube by a constant flame.

Record the time that elapses between the beginning of the heating and the moment when sufficient oxygen is being given off to rekindle a glowing splinter held at the mouth of the tube.

Mix 3 gm. of dry potassium chlorate with 1 gm. of dry manganese dioxide (weigh this accurately); place the mixture in a hard glass test-tube and heat the tube *exactly* as before. Take

the time required for sufficient oxygen to be evolved to rekindle a glowing splinter. Do not empty the tube.

Other substances can be used as catalyst, e.g. black copper oxide. Repeat the experiment with a mixture of 3 gm. of potassium chlorate and 1 gm. of black copper oxide.

Is copper oxide as good a catalyst of this decomposition as manganese dioxide?

601. Manganese dioxide as a catalyst. It is said that when manganese dioxide acts as a catalyst of this decomposition it is unchanged at the end of the reaction. If that is so, the weight of manganese dioxide left after the decomposition has been completed should be the same as that which was taken. To prove this accurately on a test-tube scale is hardly possible, but a reasonably satisfactory result can be obtained as follows.

EXPERIMENT 11. Take the tube containing 3 gm. of potassium chlorate and 1 gm. of manganese dioxide used in Exp. 10, and heat it until no more oxygen is given off. Warm the residue with water until all the potassium chloride is dissolved. Weigh a filter paper and fold it in the usual way and damp it with distilled water. Filter the liquid from the test-tube, warm the residue in the test-tube with more water and filter again. Wash all the powder out of the tube on to the filter paper; then wash the powder on the paper with several small quantities of hot water. Dry the filter paper in a steam oven or in an air oven at about 105°C . Detach the paper from the funnel and weigh it in a weighed basin, thus obtaining the weight of residual manganese dioxide. Allowing for the slight amount of manganese dioxide left in the test-tube, was the weight of the residual manganese dioxide the same as that of the original?

Chapter XL

HYDROGEN

602. Preparation from zinc and sulphuric acid. This is the usual method of preparing hydrogen in the laboratory.

EXPERIMENT 12. The apparatus shown in fig. 62 can be used, or either of those shown in figs. 58 or 59.

The one shown in fig. 62 consists of a Wolff's bottle, through one cork of which passes a thistle funnel, which must reach to the bottom of the bottle; through the other cork passes the delivery tube which communicates with the pneumatic trough.

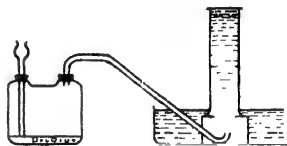


Fig. 62. Preparation of Hydrogen.

Pure zinc does not react with pure sulphuric acid, even when dilute; but the ordinary granulated zinc of the laboratory is slightly impure and reacts very well.

Theoretically 5 gm. of zinc will yield 1720 c.c. of hydrogen; you can readily collect 250 c.c. in gas jars by using 1 gm.

Whichever apparatus you use, cover the zinc with water and when all is ready add a little dilute sulphuric acid through the funnel. Allow the air to be driven out of the apparatus and then collect four jars of the gas (small ones will suffice).

Properties of hydrogen. Examine it as follows:

(1) Apply a taper. The gas burns quickly with an almost non-luminous flame.

(2) Invert a jar, pull off the greased plate and quickly insert a taper. Notice that the taper is extinguished, although the gas burns at the mouth of the jar.

(3) Over a jar place a jar of air, draw the plate away and leave

the jars together for a minute. Replace the plates on both jars and then test each with a taper. There is an explosive mixture in both of them; the hydrogen has obviously risen into the upper jar and mixed with the air.

(4) Remove the plate from another jar and leave it, mouth upwards, on the bench for half a minute. Now apply a taper. The gas in the jar does not burn or explode; all the hydrogen has escaped, because it is lighter than air.

This can be verified by attaching a small clay pipe to the hydrogen-generating apparatus and dipping the end into soap solution. Bubbles are blown and rise rapidly to the ceiling.

603. We have seen that hydrogen burns in air; what is produced by the burning?

EXPERIMENT 18. To show that water is formed when hydrogen burns in air. This can be found by either of the following pieces of apparatus, figs. 63 or 64.

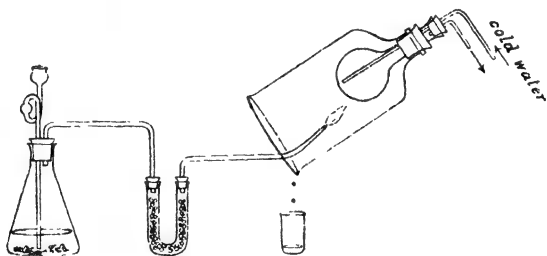


Fig. 63. Burning Hydrogen.

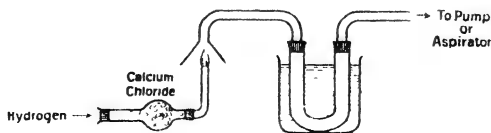


Fig. 64. Burning Hydrogen.

In either case the hydrogen from the generating flask is dried by passage through a U-tube containing calcium chloride and is

then burnt at the end of a glass tube which has been drawn out to a jet. In the apparatus shown in fig. 63 the flame is just below a flask which is kept cool by a stream of water. In that shown in fig. 64 the hydrogen burns under an inverted funnel which is connected to a U-tube cooled with water; this apparatus usually gives the better results.

A few drops of liquid collect which will change the colour of anhydrous copper sulphate from white to blue. This proves that the liquid contains a fairly high percentage of water; to prove that it is water, you will have to collect several c.c. and find the density and boiling-point of the liquid. 11 litres of hydrogen would produce about 9 c.c. of water, if nothing was lost; you will see that a large supply of hydrogen will be required to complete the proof that the liquid is water and nothing else.

EXPERIMENT 14. To show that the hydrogen combines with the oxygen of the air.

Use the apparatus shown in fig. 65.

Arrange a tube drawn out to a jet to pass through a beehive shelf in a pneumatic trough of water. Connect it to a hydrogen-generating apparatus and light the hydrogen. Invert a dry gas jar of about 300 c.c. over the flame. The hydrogen quickly goes out, and the supply should *at once* be disconnected and the end *A* of the tube *immediately* closed with your thumb. The water will rise in the gas jar. Remove the jar (this requires care) and test the residual gas with a lighted taper; it is extinguished. The hydrogen has combined with the oxygen and left the nitrogen.

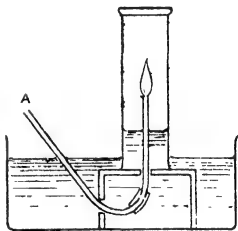


Fig. 65. Hydrogen burning in Air.

EXPERIMENT 15. To show that hydrogen will combine with the oxygen in oxides of metals.

Connect a hydrogen-generating flask to the apparatus shown

in fig. 66. Put some dry black copper oxide in the boat so that it is about two-thirds full.

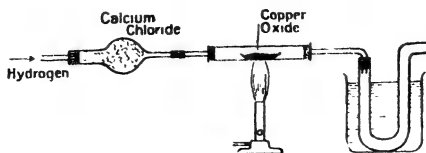


Fig. 66. Reduction of Copper Oxide.

When all the air has been driven out of the tube, but not before, light the hydrogen, and heat the copper oxide at first gently and then strongly. The oxide becomes red; when all action has ceased, allow the residue to cool in a stream of hydrogen. The residue is copper which will dissolve in nitric acid forming a blue solution with the production of brown fumes. The liquid in the U-tube answers the tests for water, already given in Exp. 13.

604. Other methods of preparation.

EXPERIMENT 16. From hydrochloric acid and (a) magnesium, (b) aluminium.

This can be done with a test-tube as in fig. 58 and a few small gas jars. 0.5 gm. of magnesium will yield more than 400 c.c. of hydrogen; 0.5 gm. of aluminium will yield more than 500 c.c.

Cover the metal with a little water and place the acid in the funnel. Add the acid a drop at a time. The action is vigorous, especially with aluminium.

If you have time you can try other metals, such as lead, tin and iron, and find whether these react with dilute hydrochloric acid or not.

EXPERIMENT 17. From steam by the action of magnesium.

For this purpose it is best to use a large flask of about 1000 c.c. capacity having a *wide* neck.

Fit the flask with a rubber bung or cork. Fit through the cork a wide tube bent at right angles and attach a piece of stiff iron wire as shown. Attach the glass tube by rubber tubing to a

delivery tube communicating with a pneumatic trough (fig. 67) and a gas jar of about 250 c.c. capacity.

Fold about 2 ft. (or 0.4 gm.) of magnesium ribbon into a small bundle, attach one end to the piece of iron wire and let the other end project. Do not put the cork into the flask.

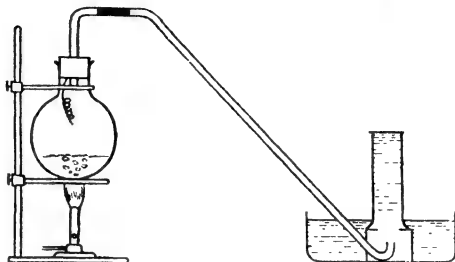


Fig. 67. Burning Magnesium in steam.

Boil the water in the flask. Ignite the magnesium ribbon with another burner and put it at once into the flask and press in the cork. The action is vigorous and hydrogen is rapidly evolved. Test the hydrogen in the usual way.

A white powder is left in the flask, which is slightly soluble in water. Filter a little of the water from the flask and test with phenolphthalein. The solution is alkaline. The white powder is magnesium oxide.

EXPERIMENT 18. From hot water by the action of the zinc-copper couple.

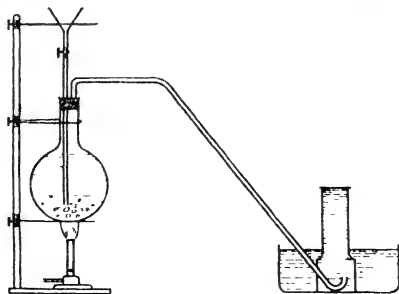


Fig. 68. Preparation of Hydrogen from water.

Prepare the zinc-copper couple by immersing about 50 gm. of zinc in a little copper sulphate solution in a porcelain basin. The zinc will quickly become coated with copper. Pour off the copper sulphate solution and wash the couple with a little water. Place it in a flask of about 250 c.c. capacity filled with water and arrange as in fig. 68.

Boil the water and collect the hydrogen which is evolved.

Chapter XLI

MEASUREMENT OF GAS VOLUMES

605. It is frequently necessary to measure in the laboratory the volume of gas evolved when a known weight of a substance takes part in a chemical reaction.

If there is no change of temperature, the apparatus shown in fig. 69 will suffice, where the gas which is set free in the test-tube *A* is collected in the graduated tube *G*. The volume of the gas evolved must be measured with the level of the water inside the graduated tube *G* the same as that outside. This is effected by slipping a crucible under the open end of *G* while it is under water and transferring the two together to a large jar of water (see fig. 70). The tube must be supported in a holder and not held in the hand.

But if heat is developed in the reaction or if heat has to be applied to the flask or tube to bring the reaction about, the air or gas in the flask will expand and some of it will be driven over into the tube. This is a very serious difficulty, as will be realised by consideration of the fact that when the temperature of a flask containing 250 c.c. of air (or other gas) is raised from 15–100° C. the air in it will expand by 78 c.c. The volume of gas collected in the measuring tube would therefore be too large. At the end of the reaction the flask must be allowed to cool so that the gas in it may regain the original temperature. If the apparatus of fig. 69 is used, water and

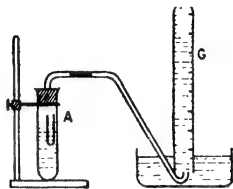


Fig. 60. Collecting a gas

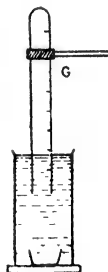


Fig. 70. Levelling.

not air or gas will be sucked back into the flask and the whole experiment ruined. The difficulty can be avoided by the use of one of the three pieces of apparatus described below. It is advisable in any case to reduce the expansion by using as small a flask (or tube) as practicable and filling it as full as possible with liquid, or solid, whose expansions are much less than that of air or any other gas. For example, if the reaction consists in heating a solid with a liquid there is usually no reason why the liquid should not fill the greater part of the flask or tube at the beginning of the reaction. Or again, if the reaction consists in heating a solid the space not occupied by the solid can be filled with glass-wool.

APPARATUS FOR MEASURING GAS VOLUMES

606. The gas burette (figs. 71 *a*, *b*). This is the most accurate apparatus. The essential point about it is that the gas is admitted

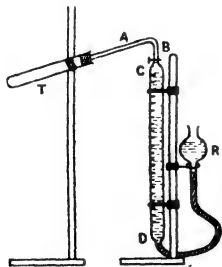


Fig. 71 *a*. Collecting in a gas burette.

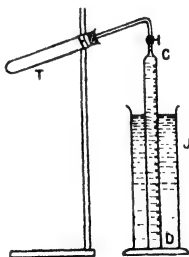


Fig. 71 *b*. A gas burette.

through the top of the measuring tube or burette. It can be closed with a glass tap; but this is not essential, a piece of rubber tubing (wired on) and a clip will suffice. It may be connected at the bottom to a reservoir of water (or mercury); but again this is not essential, as the tube can stand in a tall jar of water.

It is even more necessary in the measurement of gas volumes

than in the collection of gases to be sure that the apparatus does not leak. Ensuring this with a gas burette is very easy. The burette is filled to the top with water and the clip is closed. The apparatus in which the gas is to be generated is attached; the clip *C* is opened and the reservoir is lowered. If the water falls steadily in *CD*, there is a leak somewhere which must be detected and stopped.

At the end of the experiment, the apparatus is allowed to cool and the volume of gas is measured by bringing the water in the reservoir and tube (or in the jar and tube) to the same level.

607. A gas-measuring tube and modified form of delivery tube. The following apparatus using an ordinary graduated gas-measuring tube has been found to give very satisfactory results. If a preliminary experiment (see below) has given an indication of the volume of gas which will probably be obtained from a given weight of substance, the apparatus shown in fig. 72 can be used. As the graduated tube must be placed in a tall jar when the gas is measured, it is best to have it there from the start. The delivery tube *CFD* is bent as shown in fig. 72. The end *C* is closed with rubber tubing and a clip *E*. The top *D* of *CFD* is below the top of the jar of water; *G* having been filled with water can be slipped over *DF* without any difficulty. The weight of substance taken must be such as to ensure that the volume of gas evolved will drive the water below *D*.

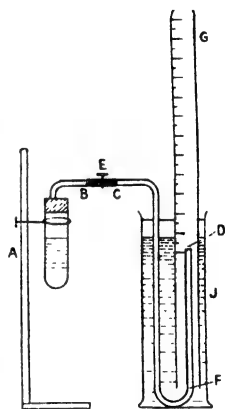


Fig. 72. Apparatus for measuring volume of gas evolved.

When the flask (or tube) in which the gas is to be generated is ready, it is attached to *C* and the clip *E* is opened. If *DF* remains full of air, all is in order; but if the water fills *DF* and part of the other limb of the delivery tube, there is a leak which must be

repaired before any attempt is made to go further. When the leak has been repaired, the delivery tube must be refilled with air.

The gas having all been collected, the apparatus is allowed to cool. Cooling will have finished when the volume of gas in *G* no longer contracts. To measure the volume of the gas, *G* is raised (with a test-tube holder or in a clamp) until the water in it is level with the top of the jar, which is then filled with water.

A larger graduated tube is shown in fig. 73.

PRELIMINARY EXPERIMENT. A preliminary experiment can be carried out with a delivery tube such as is shown in fig. 74. In this case the delivery tube extends to the top of the graduated tube. The insertion of this delivery tube into *G* can be effected without much difficulty. The clip *E* having been

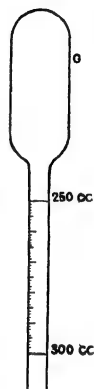


Fig. 73. A larger graduated tube.

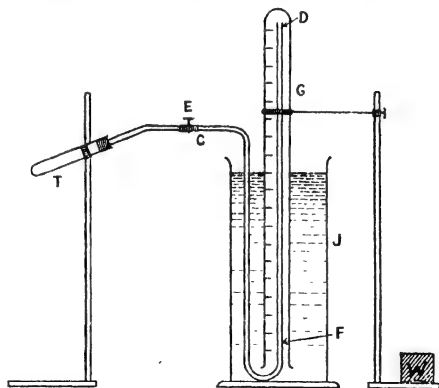


Fig. 74. Apparatus for measuring the volume of gas evolved.

closed, *DF* is inserted into *G* which is full of water. *G* can then be almost closed with the thumb before it is inverted in a

jar of water. A small bubble of air will pass up the tube and can be allowed for if desired, but, as the experiment is a preliminary one, strict accuracy is not looked for. The volume of gas collected can be measured as described above; the part of the delivery tube which extends above the water will make the apparent volume of gas collected somewhat too large.

608. The syphon bottle. This is the apparatus most frequently used in school laboratories. It has the very great advantage that a large quantity of gas can be dealt with, as the capacity of a Winchester quart bottle, which is generally used, is about 2.5 litres. This enables a comparatively large quantity of substance to be used and reduces the percentage error in weighing. Success cannot be achieved unless all leaks have been detected and repaired.

A Winchester quart or other large bottle (fig. 75) is fitted with a rubber bung or very well-fitting cork, through which pass two tubes, one *AB* just passing through the bung, the other *HD* reaching to the bottom of the bottle. *HD* is connected to another tube *F* which reaches to the bottom of a graduated cylinder *G*. To the end of *AB* is attached a piece of rubber tubing and a clip *E*.

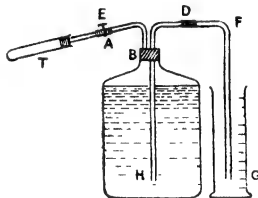


Fig. 75. The syphon bottle.

Note. It is essential that the bung shall fit well and that the tubes shall be tight in the bung and in the rubber tubing.

The apparatus must be tested for leaks. To do this, fill the bottle with water and insert the bung with the tubes. Do not attach the tube *T*. Blow down *AB* and force water through *HDF* into the cylinder *G*, so that the end of *F* is covered. Close the clip *E*. If no more water syphons over into *G*, there is no leak. If any more water syphons over, there is a leak, which must be found and stopped.

After the bottle has been proved free from leaks, it will be

necessary to ensure that the remainder of the apparatus is gas-tight. When the flask or tube in which the gas is to be generated is ready, it is connected to the rubber tubing and the clip *E* is opened; if water syphons into *G*, there is a leak and this must be found and repaired.

When the reaction is finished, the apparatus is allowed to cool, *G* is raised or lowered until the water in it is at *the same level* as the water in the bottle and the volume of water which has been driven out of the bottle is recorded.

609. Determination of the density of oxygen, or determination of the volume of oxygen at S.T.P. obtained by heating 1 gm. of potassium chlorate.

EXPERIMENT 19. For this experiment a clean and dry hard glass test-tube about 12 cm. long and 15 mm. bore is fitted with a rubber bung carrying a piece of glass tubing with which it can be connected to one of the pieces of gas-measuring apparatus shown in figs. 71, 72, or 75. Weigh accurately a suitable quantity of dry potassium chlorate, bearing in mind that 1 gm. will yield about 275 c.c. of oxygen at N.T.P. If your measuring tube will hold 100 c.c., use about 0.25 gm.; if you are working with a syphon bottle, you can use 3 or 4 gm. Mix the chlorate with about $\frac{1}{3}$ its weight of manganese dioxide and put the mixture in the tube *T*, fill the remainder of the tube loosely with glass-wool and then weigh the whole tube. Connect *T* to the measuring apparatus, testing for leaks as described before. (Take any readings of volume which may be necessary with the syphon bottle.) Heat *T* (gently at first) until all the oxygen has been driven off. When the evolution of oxygen has ceased, allow *T* to cool and read the volume of gas evolved, after ensuring that the two levels of water are the same. Record the temperature of the water over which the gas is collected and also the height of the barometer. The gas has been collected over water and is therefore saturated with water vapour; the pressure of the gas alone is the height of the barometer minus the vapour pressure of water at

the temperature of the experiment. Correct the volume of gas to S.T.P.

When the volume of gas has been measured, remove *T* and weigh it again. The loss of weight is the weight of oxygen which has been driven off. Hence calculate the weight of 1 litre of oxygen at S.T.P.

As a known weight of potassium chlorate was taken, calculate the volume of oxygen at S.T.P. which can be obtained from 1 gm. of potassium chlorate.

Chapter XLII

EQUIVALENT WEIGHTS, LAWS OF DEFINITE AND MULTIPLE PROPORTIONS

EQUIVALENT WEIGHTS

610. There are many methods of determining equivalent weights, some of which are suitable for certain elements but are unsuitable for others. A few of the methods are described below, these being chosen as suitable for school work; but it should be remembered that these are only a selection.

611. By displacement of hydrogen from an acid or an alkali.

EXPERIMENT 20. Use any one of the pieces of gas-measuring apparatus already described and shown in figs. 71, 72 and 75. Those shown in figs. 71 and 75 must be modified by substituting for the test-tube the arrangement shown in fig. 76. Put the acid in a test-tube *T* and weigh the metal (which should have been carefully cleaned) in a short test-tube *S*. Lower this tube carefully (not by cotton) into the acid (fig. 76). The apparatus having been tested for leaks, tilt *T* so that acid runs into *S*. If the metal will not dissolve in the cold acid, heat *T*; but remember to allow *T* to cool again before measuring the volume of hydrogen. Be careful to "level" the hydrogen, record

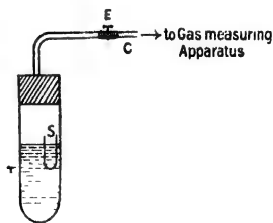


Fig. 76. Displacement of Hydrogen from an acid or an alkali.

the volume, the temperature and the height of the barometer. Record your results as follows:

Weight of metal	=gm. (M).
Volume of hydrogen	=c.c. (V).
Temperature	=°C. (t).
Height of barometer	=mm.
Vapour pressure of water at t° C.	=mm.
Pressure of hydrogen	=mm. (p).
Volume of hydrogen at s.t.p.	

Since 1 litre of hydrogen at s.t.p. weighs 0.09 gm., V_0 c.c. of hydrogen at s.t.p. weigh

$$\frac{V_0 \times 0.09}{1000} \text{ gm.}$$

$V_0 \times 0.00009$ gm. of hydrogen were displaced by M gm. of metal; hence calculate the weight of metal which will liberate 1 gm. of hydrogen from an acid. This is the equivalent weight (in grammes) of the metal (see § 106).

Hydrochloric acid is usually employed, but dilute sulphuric acid may be used.

Notes (i) The following table gives the exact equivalent weights of four metals and also the weight of each metal which will displace 100 c.c. of hydrogen from an acid.

	Exact equiv. wt.	Wt. which will displace 100 c.c. of hydrogen gm.
Aluminium	8.99	0.0802
Magnesium	12.16	0.1086
Iron	27.92	0.2493
Zinc	32.69	0.2918

It is evident from these figures that if your measuring apparatus has a maximum capacity of 100 c.c. you cannot expect to get a

result accurate to 1 per cent., when you use aluminium or magnesium, unless you have a *very good* balance and can weigh very accurately. With such an apparatus you should use iron or zinc. Fairly satisfactory results can be obtained with aluminium and magnesium if the measuring apparatus has a capacity of 300 c.c. and the balance will weigh accurately to 0.01 gm. If your balance will not weigh to a greater accuracy than 0.1 gm. you must use the syphon bottle.

(ii) Pure zinc dissolves somewhat slowly in dilute acids and requires to be heated.

(iii) With a suitable apparatus and balance the equivalent of aluminium may be determined by dissolving it in caustic soda solution. In this case the aluminium may be placed directly in the caustic soda solution, as no action occurs until the soda is heated.

612. By displacement of a metal (of known equivalent weight) from a solution of a salt by another metal. Iron will displace copper from solutions of copper sulphate.

EXPERIMENT 21. Weigh accurately about 1 gm. of dry reduced iron into a beaker; pour on to the iron a hot solution of copper sulphate containing approximately 7 gm. of crystallised copper sulphate in 100 gm. of water. Stir well for 5 min. and filter through a weighed filter paper. Wash all the copper on to the filter with hot water and finally rinse with industrial spirit. Dry the filter in an oven and weigh it. Subtract the weight of the filter paper. From the weights of iron taken and copper obtained, calculate the weight of iron which will displace 31.8 gm. of copper. This is the equivalent weight of iron.

613. By conversion of a metal into its oxide. The direct method of heating the metal in air or oxygen cannot be applied in many cases, as the metal is usually not completely converted into the oxide. Magnesium will burn in oxygen or in air; but when it burns in air a considerable proportion of nitride is formed with the oxide.

An indirect method consists in heating the metal with nitric acid. This may be done with tin or with copper. In the former case, a compound metastannic acid is first formed, which on heating is converted into the oxide; in the case of copper the nitrate is first formed, which on heating is converted into the oxide.

EXPERIMENT 22. Heat a clean crucible (with lid) to redness and allow it to cool in a desiccator. Weigh it. Heat it again, cool it and weigh it again. Repeat this process until its weight is unchanged. Place in it about half a gramme of copper foil (or tin foil) and weigh again. Lift the lid a little and add concentrated nitric acid drop by drop from a pipette (do not suck the liquid into the pipette; dip the pipette into the acid and close its upper end with your finger). As soon as the action stops, heat the crucible gently at first and then to redness. Allow it to cool in a desiccator and then reweigh it. Add a few more drops of acid to the residue and reheat the crucible and reweigh it. When the weight is constant all the metal will have been converted into oxide.

Record your results as follows:

Weight of crucible and copper	=gm.
Weight of crucible	=gm.
Weight of copper	=gm. (<i>M</i>).
Weight of crucible and copper oxide	=gm.
Weight of crucible	=gm.
Weight of copper oxide	=gm. (<i>S</i>).

S - *M* gm. of oxygen have combined with *M* gm. of copper. Calculate the weight of copper which would have combined with 8 gm. of oxygen.

The difficulty with the above method is the creeping of the acid (and solution) over the edges of the crucible. This can be avoided by the following method.

EXPERIMENT 23. Weigh a dry test-tube with a plug of glass-wool; weigh it again with about a gramme of pure copper. Add nitric acid and place the plug of glass-wool in the open end of the tube. Evaporate at a *sloping angle* until only black oxide remains. Weigh when cool.

Tin and zinc may be dealt with in the same way. The flame used should be from 1 to 2 in. long and just non-luminous.

Record your results as shown in the example in Exp. 22.

614. By reduction of the oxide of the metal by heating it in a current of hydrogen or coal gas.

EXPERIMENT 24. A porcelain boat is heated gently in a Bunsen burner and then allowed to cool in a desiccator. It is then weighed carefully. Dried copper oxide is placed in the boat until it is about two-thirds full; the boat is again weighed. It is placed in a hard-glass tube arranged as shown in fig. 77. The tube should be inclined slightly downwards towards the end *B*, so that the water



Fig. 77. Equivalent of a metal by reduction of its oxide.

which is formed will not run back on to the hotter part of *T* and cause it to crack. Coal gas or hydrogen is passed through the tube *T*, and after it has been passing for about a minute and has displaced the air, it is lighted at the jet *C*. *T* is then gently heated, and when it is warm the heating is concentrated at one end of the boat *E*. The black colour of the oxide will change at the heated end to red; heating is then continued further along until all the black oxide has been changed to red copper. The tube is then allowed to cool with the gas still passing. When it is cold the boat is removed and weighed. It is then replaced in the tube, which is again *filled with gas as before*, reheated, cooled and reweighed. If the second heating has produced a further

reduction in weight, the process must be repeated until the weight is constant.

Record your results as follows:

Weight of boat and copper oxide	=gm.
Weight of boat	=gm.
Weight of copper oxide	=gm. (<i>S</i>).
Weight of boat and copper	=gm.
Weight of boat	=gm.
Weight of copper	=gm. (<i>M</i>).

S -- *M* gm. of oxygen have been found to be combined with *M* gm. of copper; hence calculate the weight of copper which is combined with 8 gm. of oxygen in black copper oxide. This is the equivalent weight.

EXPERIMENT 25. An easier method is the following: a small hole is blown in the side of a narrow test-tube ($\frac{1}{4}$ – $\frac{5}{8}$ in.) near the closed end. This is conveniently done by closing the tube with a cork or with the finger and heating with a fine blowpipe jet.

The tube is weighed; a quantity (3–4 gm.) of dried copper oxide is placed in the tube, which is kept on its side; the upper part is wiped out and the tube is reweighed. The tube is conveniently connected to the gas supply by pushing the gas tubing into the open end of the tube; the gas is turned on and, after passing for about a minute to displace the air, is lighted as it issues from the small hole (see fig. 78). The tube is then heated with a Bunsen burner until the oxide is reduced. After cooling in the gas stream, the tube is reweighed and then reheated until the weight is constant.

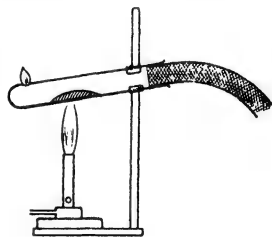


Fig. 78. Reduction of an oxide.

Record your results as before and calculate the weight of copper which would be combined with 8 gm. of oxygen.

Iron oxide can be reduced in a similar way. Good results can be obtained for lead oxide, if the oxide is placed on a strip of copper foil and not in direct contact with the glass.

VERIFICATION OF THE LAW OF DEFINITE PROPORTIONS

615. The methods of Exps. 24 and 25 can be applied to the verification of the Law of Definite Proportions. For this purpose two quantities of copper oxide are required which have been prepared by *different methods* (this is essential). Copper oxide can be prepared by heating either copper nitrate or copper carbonate.

EXPERIMENT 26. Heat about 15 gm. of copper nitrate in a basin in a fume cupboard; when red fumes cease to be evolved, allow the basin and its contents to cool in a desiccator and then weigh them. Repeat the heating, cooling and weighing until the weight is constant.

Also heat about 7.5 gm. of copper carbonate in a similar way (not necessarily in a fume cupboard) for 10 min. Allow to cool in a desiccator and weigh. Repeat the process until the weight is constant.

In this way you have obtained about 5 gm. of each of two specimens of copper oxide prepared by different methods.

Determine either the equivalent weight of copper in each specimen or if you prefer it the percentage of copper in each specimen by the methods of Exp. 24 or 25. Remember that the copper oxide must be accurately weighed in each case. If you use the method of Exp. 24, you can put both boats in the same tube and carry out the reductions simultaneously.

VERIFICATION OF THE LAW OF MULTIPLE PROPORTIONS

616. The methods of Exps. 24 and 25 can also be applied to verification of the Law of Multiple Proportions.

EXPERIMENT 27. For this purpose specimens of black copper oxide and of red copper oxide are required. The black copper oxide must be dried by heating in a basin till its weight is constant. The red copper oxide must be freshly prepared (see note at end). Portions of each of the oxides are weighed accurately and then reduced in a stream of hydrogen or coal gas as described in Exps. 24 and 25. The copper must be allowed to cool in a current of the gas and the heating repeated until the weight is constant.

Calculate in each case the equivalent weight of copper or (if you prefer it) the weight of copper combined with 1 gm. of oxygen and then find the ratio of the weights which you have calculated.

Preparation of the red oxide of copper (cuprous oxide). Fehling's solution is made by mixing a solution of copper sulphate with a mixed solution of sodium potassium tartrate and caustic soda. If this solution is warmed with a solution of grape sugar (glucose), a red precipitate of cuprous oxide is formed. Filter this off, wash it with distilled water and dry on a filter paper in a desiccator.

Chapter XLIII

NITROGEN

617. Preparation from air. Air contains approximately 79 per cent. by volume of nitrogen mixed with oxygen, water vapour, carbon dioxide and the inert gases helium (in very small quantity), neon, argon, xenon and krypton. On a commercial scale nitrogen, mixed with the inert gases, is prepared from air by careful distillation of liquid air. This process is not possible in a school laboratory and other methods are therefore used.

The carbon dioxide can be removed by passing the air through caustic soda solution, and the water vapour can be removed by passage through a bottle of strong sulphuric acid or a U-tube containing anhydrous calcium chloride. The oxygen can be removed by one of the following methods:

- (a) passing the air over red-hot copper;
- (b) passing the air over burning phosphorus.

The latter is the more effective method.

In the methods described below the gas is collected over water and therefore no measures are adopted for removing the water vapour.

EXPERIMENT 28. Preparation of nitrogen from air by means of copper.

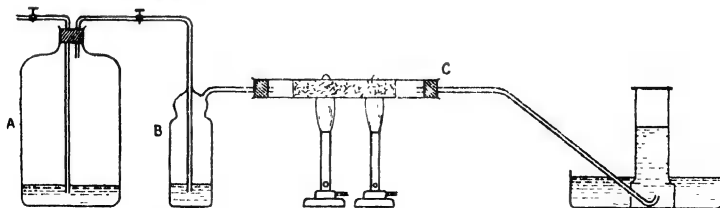


Fig. 79. Preparation of Nitrogen from Air—by Copper.

The tube C (fig. 79) is loosely packed with copper turnings.

will then be seen that the other aspirator is no longer empty but contains about one-fifth of its volume of water, which represents the volume of oxygen absorbed by the phosphorus.

The nitrogen can be transferred into gas jars by running water from the tap into the aspirator and collecting the gas in jars in a pneumatic trough as shown in fig. 81.

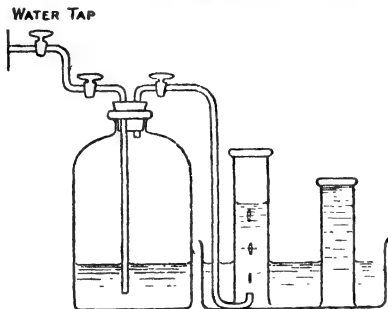


Fig. 81.

618. Preparation from compounds of nitrogen. Pure nitrogen can be obtained from many compounds of nitrogen. The easiest method is the following:

EXPERIMENT 30. Warm a solution of 15 gm. of ammonium chloride and 15 gm. of sodium nitrite in 60 c.c. of water in a small generating flask (see fig. 82) and collect the gas over water; this will yield about 4200 c.c. of gas. Or warm a solution of 1 gm. of each of the above substances in 5 c.c. of water in a boiling tube or a small flask of about 50 c.c. capacity; this will yield about 300 c.c. of gas.

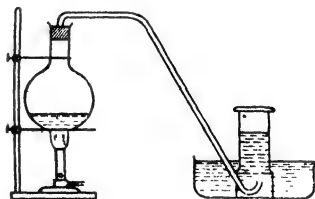


Fig. 82. Preparation of Nitrogen.

Properties of nitrogen.

Test the gas with (a) a lighted taper, (b) burning phosphorus, (c) burning sulphur.

The gas might be confused with carbon dioxide, but note that it is comparatively insoluble in water. Also shake a small jar full of it with 5 c.c. litmus solution and another jar-full with a few c.c. of lime water. Note carefully how to distinguish between nitrogen and carbon dioxide.

Nitrogen will combine directly with magnesium, calcium and cerium, if these metals are heated in the gas. The combination with magnesium can be shown by heating about 2 ft. of magnesium ribbon in a crucible with a lid, occasionally lifting the lid until all the magnesium has been burnt. Remove the solid from the crucible into a gas-generating tube and add about 5 c.c. of water. Boil the water and hold in the mouth of the tube a strip of filter paper which has been soaked in Nessler's solution. A brown coloration indicates that the gas contains ammonia, which was produced from a compound of nitrogen and magnesium called magnesium nitride, Mg_3N_2 :



Similar results are obtained if calcium or cerium is heated in a crucible and the resulting solid is treated as above.

Chapter XLIV

ANALYSIS OF MIXTURES OF GASES

619. The analysis of mixtures of gases is an important part of the work of a chemist; it is obviously of very great importance in gas works and in other industries where special attention must be given to the composition of the gases which are being produced; it is frequently of importance in considering the ventilation of buildings and the regulation of draughts in furnaces and chimneys. The apparatus used may be somewhat complicated; that which is described here is of a very simple type and is intended only to indicate the principles involved.

This can best be done by considering an example. Suppose that the gaseous mixture consists of nitrogen and oxygen. The proportions by volume of the two constituents can be determined by taking a measured volume of the mixture and absorbing the oxygen by an alkaline solution of pyrogallol and measuring the volume of the residual nitrogen.

There are two methods of doing this. In the first the measured volume of the mixture is forced out of the measuring tube or burette into a vessel full of the absorbent, shaken thoroughly and then returned to the measuring tube or burette where the volume of gas which has not been absorbed is measured. In the second method the absorbent is introduced directly into the measuring tube, and this is the one which we shall describe.

620. Determination of the percentage of oxygen in air.
(a) By alkaline pyrogallol.

EXPERIMENT 81. The quantity of air to be analysed is contained in a graduated gas-measuring tube *G* (see fig. 83). A cork is inserted (under water) carrying two tubes *CD* and *BK* both closed with rubber tubing and clips and both full of water. The tube *G*

is placed in a tall jar of water and one of the clips is opened under water. The volume of air is read with the precautions described in § 605 and the clips closed.

G is removed from the jar and a thistle funnel arranged as shown in the figure and full of an alkaline solution of pyrogallol is connected to *D*. The clips *E* and *D* are opened; the opening of *K* will allow the water to run out and the pyrogallol to enter *G*. The three clips having been closed and the thistle funnel removed, *G* is shaken for several minutes to allow the reagent to absorb the oxygen. *D* is opened under water and the volume of residual nitrogen is measured. The percentage of volume of oxygen in the air can then be calculated.

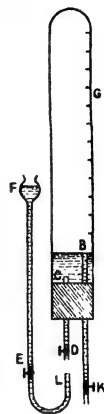


Fig. 83. Analysis of a mixture of gases.

621. Analysis of a mixture of nitrogen, oxygen and carbon dioxide. EXPERIMENT 31A. In this case the carbon dioxide must be absorbed first by shaking with caustic soda in a manner similar to that described above. The caustic soda must then be replaced by an alkaline solution of pyrogallol. In order that this may be done, *BK* must be pushed further through the cork so that *B* is just below the surface of the liquid in *G*. It is best to remove the cork under water before attempting to push *BK* further through the cork. The cork having been replaced in *G*, the liquid which is in *G* can be replaced by an alkaline solution of pyrogallol (using the thistle funnel as before) and the oxygen absorbed.

622. Determination of the percentage of oxygen in air.

(b) **By phosphorus.** The percentage by volume of oxygen in a mixture containing that gas can be determined by absorbing the oxygen with phosphorus. A simple method of doing this is the following.

EXPERIMENT 32. Put a few pieces of phosphorus in some water in a test-tube and place the tube in warm water in a beaker, until the phosphorus melts. Take a piece of wire about 4 in. longer than the graduated tube and twist the end. Put the twisted end into the molten phosphorus in the test-tube and *cool* the tube. Pour a few c.c. of water into the graduated tube. When the phosphorus has cooled, pull it out of the test-tube and put it at once into the water in the graduated tube; bend the wire over the end of the tube, close the latter with the thumb and invert the tube in the gas jar. The arrangement is now as shown in fig. 84. Holding the tube in a test-tube holder, bring the surfaces of the water inside and outside the tube to the same level and read the volume of air. Leave the tube for about 24 hours and then re-level as before and read the volume of residual gas. The difference is the volume of oxygen absorbed by the phosphorus.

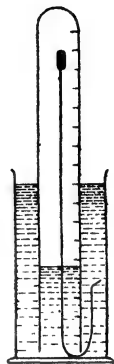


Fig. 84. Composition of Air—by Phosphorus.

Chapter XLV

ACIDS, BASES AND SALTS

ACIDS

623. Properties of acids. There are three acids which are commonly called "mineral acids"; they are sulphuric, hydrochloric and nitric acids. You have already seen that sulphuric acid and hydrochloric acid evolve hydrogen if a dilute solution is treated with zinc or iron or magnesium. Cold dilute nitric acid (1 in 5) evolves hydrogen if it is treated with magnesium but not with zinc or iron. There are many other acids besides the three mentioned above, and a number of these evolve hydrogen when their solutions are treated with magnesium.

EXPERIMENT 33. To examine the action of magnesium on acetic, formic, oxalic, citric, tartaric and benzoic acids.

Place about 0.3 gm. of magnesium ribbon or powder in a boiling-tube or small flask; add the acid a little at a time through the funnel and collect the gas in a small gas jar (see fig. 58).

624. The question may be asked, What is produced in addition to hydrogen? The answer given in chap. xv, § 142 is that a salt is produced. This will be investigated.

EXPERIMENT 34. Preparation of magnesium sulphate from metallic magnesium.

Place 20 c.c. of the bench dilute sulphuric acid in an evaporating basin and add powdered magnesium a little at a time until no more will dissolve. (Caution: hydrogen is given off freely; do not allow any flames to be brought near the basin.)

Filter off any undissolved magnesium; evaporate the solution carefully. From time to time dip a glass tube into the basin and transfer a drop of the solution to a watch-glass. If crystals form

on cooling, allow the liquid in the basin to cool and pour it into a beaker, leaving the crystals in the basin. Scrape the crystals on to a pad of filter paper and dry them by covering them with another pad of paper. White crystals of Epsom Salts (or magnesium sulphate) are obtained.

625. While a number of acids evolve hydrogen when they are treated with magnesium, zinc or iron, there are other acids which will not do so. We must now find some other tests which characterise all the acids.

EXPERIMENT 35. Tests for acids.

For this purpose we require dilute solutions of sulphuric, hydrochloric, nitric, acetic, formic, oxalic, citric and tartaric acids.

(a) Add to 1 c.c. of each in turn (i) two drops of litmus solution, (ii) two drops of methyl orange solution, (iii) two drops of phenolphthalein solution, and observe the changes in colour.

(b) Add 2 c.c. of each in turn to 2 c.c. of sodium carbonate solution in a test-tube fitted with a cork and delivery tube (see fig. 85) and pass the gas into lime water.

(c) Add 1 c.c. of each in turn to a small piece of sodium sulphide; warm if necessary and smell the issuing gas.

(d) Pour into a test-tube 1 c.c. of a solution of potassium iodide (containing about 33 gm. per litre) and 1 c.c. of a solution of potassium iodate (containing about 7 gm. per litre); add a few drops of the solution of one of the acids. If the liquid turns brown, test it with starch paper; a blue or black colour will indicate that the brown colour of the solution was caused by iodine.

Test each acid in turn. You will thus have learnt that acids (a) react in certain ways with litmus, methyl orange, and

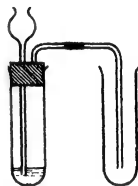


Fig. 85. Action of an acid on Sodium Carbonate.

phenolphthalein, (b) liberate carbon dioxide from sodium carbonate, (c) evolve sulphuretted hydrogen with sodium sulphide, and (d) liberate iodine from mixed solutions of potassium iodide and potassium iodate.

BASES

626. Properties of bases. Some bases are soluble in water and are called alkalis. Such are sodium hydroxide, potassium hydroxide, calcium hydroxide (or slaked lime) and barium hydroxide. These substances have certain distinctive properties which can easily be demonstrated.

EXPERIMENT 36. For this purpose we require dilute solutions of the above substances.

Add to 1 c.c. of each in turn (a) two drops of purple litmus solution, (b) two drops of methyl orange solution, (c) two drops of phenolphthalein solution, and observe the changes in colour.

It is easy to show that they destroy the characteristic properties of mineral acids.

EXPERIMENT 37. (i) Place 10 c.c. of the bench dilute hydrochloric acid solution in an evaporating basin and add sodium hydroxide solution carefully until a drop of the liquid taken on a glass rod does not make a red stain on a piece of blue litmus paper. Then test portions of the liquid with (d) sodium carbonate solution, (e) a fragment of solid sodium sulphide, (f) 1 c.c. each of potassium iodide solution and potassium iodate solution.

PREPARATION OF SALTS

627. The question now to be answered is, What has been formed by the action of hydrochloric acid on sodium hydroxide?

EXPERIMENT 37 (cont.). Evaporate the remainder of the solution carefully (see § 624) until crystals are formed. These crystals will be found to be identical with those of common salt, if both are examined with a lens (or magnifying glass).

Repeat, using (ii) sodium hydroxide and sulphuric acid, (iii) potassium hydroxide and nitric acid. In each case crystalline solids are obtained. The crystals obtained in Exps. 37 (i) and (ii) should be kept for further use.

628. The soluble hydroxides or alkalis are very few in number, but there are three other classes of compounds from which salts can be obtained by dissolving them in acids. They are the insoluble hydroxides, the oxides and the carbonates of metals. They are not soluble in water and do not affect litmus, methyl orange or phenolphthalein as the alkalis do; but when they dissolve in acids they form salts.

The first method of preparing salts is by dissolving a metal in an acid (Expts. 34, 42 and 43); the second consists in dissolving an oxide or hydroxide of a metal in dilute acid.

A few examples are given below:

EXPERIMENT 38. Preparation of magnesium sulphate from magnesium oxide.

Place 20 c.c. of the bench dilute sulphuric acid in an evaporating basin, warm it gently and add magnesium oxide a little at a time until no more will dissolve. Filter off any undissolved magnesium oxide, evaporate the solution carefully (see § 624) until crystals are obtained. Allow the liquid to cool and pour it into a beaker, leaving the crystals in the basin. Scrape the crystals on to a pad of filter paper and dry them by covering them with a piece of paper and pressing them. Examine the crystals to see whether they are the same as those obtained by dissolving magnesium in dilute sulphuric acid in Exp. 34.

629. You will see that the same salt is obtained when

(a) the metal is dissolved in an acid,

(b) the oxide of the metal is dissolved in the acid,

the only difference being that in the first case hydrogen is liberated, but not in the second. As water is known to be an oxide of hydrogen (see §§ 44 and 82), we may reasonably

surmise that the hydrogen of the acid and the oxygen of the oxide combine to form water in the second case. This hypothesis can only be tested by passing a current of a dry acid gas over a dry oxide of a metal and showing that water is formed in addition to a salt; this is done in Exp. 61 (9).

Two other examples of the same method may be given.

EXPERIMENT 39. Preparation of copper sulphate from copper oxide.

Place 20 c.c. of the bench dilute sulphuric acid in an evaporating basin, warm it gently and add copper oxide a little at a time until no more will dissolve. Filter off any copper oxide which remains undissolved and proceed as before. Blue crystals of copper sulphate are obtained.

EXPERIMENT 40. Preparation of lead nitrate from lead oxide.

Take 20 c.c. of the bench dilute nitric acid, heat it nearly to boiling and proceed as before.

630. The third method of preparing salts consists in dissolving a carbonate of a metal in dilute acid. In this method carbon dioxide is evolved.

EXPERIMENT 41. (a) Preparation of copper sulphate from copper carbonate.

Proceed as in Exp. 38, using copper carbonate instead of magnesium oxide, but be careful not to add a large excess of carbonate.

(b) Preparation of lead nitrate from lead carbonate.

Take 20 c.c. of the bench dilute nitric acid and warm it. Add lead carbonate a little at a time until no more will dissolve; avoid adding a large excess of carbonate. Proceed as before.

631. We have now considered three methods of preparing salts:

(1) by dissolving a metal in an acid;

(2) (a) by neutralising a soluble hydroxide (alkali) with an acid;

(b) by dissolving the hydroxide or oxide of a metal (even if it is insoluble in water) in an acid;

(3) by dissolving the carbonate of a metal (even if it is insoluble in water) in an acid.

The first method (dissolving a metal in an acid) is not usually as successful as the other two, as acids dissolve metals more slowly than they dissolve hydroxides, oxides or carbonates.

Note. The formation of salts by the action of a metal on an acid is not limited to those cases in which hydrogen is evolved. When nitric acid is used, oxides of nitrogen are evolved; and when concentrated sulphuric acid is used, sulphur dioxide is evolved.

EXPERIMENT 42. Preparation of copper nitrate from copper and dilute nitric acid.

Do this in a fume cupboard. Place about 5 gm. of copper turnings in an evaporating basin and add slowly some nitric acid which has been diluted with an equal volume of water. Continue adding the acid until the copper has *nearly* all dissolved. Wait until all action has ceased, pour off the clear liquid into a clean basin and evaporate to crystallisation in the usual way. Dry the crystals on filter paper.

EXPERIMENT 43. Preparation of copper sulphate from copper and concentrated sulphuric acid.

Do this in a fume cupboard. Place about 5 gm. of copper turnings in a large evaporating basin and add a small quantity of concentrated sulphuric acid. Warm the liquid carefully. Proceed as above taking care not to dissolve all the copper. Allow the liquid to cool and add about 100 c.c. of distilled water, stir and warm the liquid. Filter it while hot into a clean basin and evaporate to crystallisation in the usual way.

632. Insoluble salts. There is a fourth method which is of general importance; by this an insoluble salt of a metal can be prepared. A solution of a soluble salt containing the required metal is mixed with a solution of the required acid or of a soluble salt of the required acid. The insoluble salt of the metal is obtained by double decomposition. To take the two examples described below:

Lead nitrate (soluble) + potassium iodide (soluble) form lead iodide (insoluble) + potassium nitrate (soluble).

Lead nitrate (soluble) + sulphuric acid (soluble) form lead sulphate (insoluble) + nitric acid (soluble).

Note. All nitrates are soluble in water and it is therefore best to use the nitrate of the metal; all sodium salts and nearly all potassium salts are soluble and it is therefore best to use the sodium or potassium salt of the required acid (see §§ 524 and 525).

EXPERIMENT 44. Preparation of lead iodide.

Make a solution of about 1.6 gm. of lead nitrate in 50 c.c. of water and add 50 c.c. of potassium iodide solution (containing 33 gm. per litre). A yellow precipitate of lead iodide is obtained. Filter off the precipitate and wash it several times with distilled water while still on the filter paper. Dry the precipitate and paper in a steam oven or air oven at 105° C.

As lead iodide is soluble in hot water, it can be obtained as yellow crystals by dissolving the precipitate (after filtering and washing but without drying) in a large quantity of boiling water and allowing the solution to cool.

EXPERIMENT 45. Preparation of lead sulphate.

Make a solution of about 4 gm. of lead nitrate in 50 c.c. of water; add to it dilute sulphuric acid until no further formation of precipitate can be detected. The precipitate is lead sulphate. Filter this off; when all the precipitate has been transferred to the filter paper, wash it several times with distilled water. Dry it with the filter paper in a steam oven or in an air oven at 105° C.

633. Acid salts. In the preparation of sodium chloride by the reaction between hydrochloric acid and sodium hydroxide solution (Exp. 37 (i)) the latter was added until the acid ceased to redden blue litmus and to show the other reactions of an acid. That is to say, the acid was neutralised. A similar method was adopted in Exp. 37 (ii) in the preparation of sodium sulphate from dilute sulphuric acid and sodium hydroxide solution.

Would the same salts have been obtained if the amount of sodium hydroxide added had been only one-half of that required for neutralisation?

EXPERIMENT 46. Preparation of acid salts.

Measure from a measuring cylinder 10 c.c. of the bench dilute hydrochloric acid and add sodium hydroxide solution until the liquid is neutral. Then add another 10 c.c. of the same solution of hydrochloric acid. You thus have a solution of hydrochloric acid to which has been added only one-half of the amount of sodium hydroxide solution necessary for neutralisation. Evaporate the liquid (in a fume cupboard) to crystallisation and compare the crystals with those which were prepared in Exp. 37 (i).

EXPERIMENT 47. Preparation of acid sodium sulphate (sodium bi-sulphate or sodium hydrogen sulphate).

Repeat Exp. 46, using 10 c.c. of bench dilute sulphuric acid, neutralising it with sodium hydroxide solution and then adding a further 10 c.c. of the same solution of sulphuric acid. Compare the crystals which are obtained with those which were prepared in Exp. 37 (ii).

634. You will now realise that hydrochloric acid yields the same salt whether it reacts with an amount of sodium hydroxide solution sufficient for neutralisation or with only half that amount. There is in fact only one compound obtainable by the reaction of hydrochloric acid with sodium hydroxide.

On the other hand sulphuric acid yields different salts according as it reacts with an amount of sodium hydroxide sufficient

for neutralisation or with only half that amount. There are two compounds obtainable by the reaction of sulphuric acid with sodium hydroxide.

Note. What is true of reactions with sodium hydroxide is true also of reactions with potassium hydroxide as is explained in § 506.

The salt obtained when sulphuric acid reacts with an amount of sodium hydroxide solution sufficient for neutralisation is called a normal salt; that obtained when sulphuric acid reacts with only half that amount is called an acid salt (see § 166).

Chapter XLVI

VOLUMETRIC ANALYSIS

ACIDS AND ALKALIS

635. The reader will remember from his perusal of chap. xvi that the object of volumetric analysis is to determine the quantitative composition of substances or of solutions by means of reagents of known concentration. For example, it is there explained how the concentration of a solution of an alkali can be determined by finding the volume of a solution of an acid of known concentration which will react with a measured volume of the alkaline solution. The question will immediately arise, "How can we tell when the quantity of alkali which we have taken has completely reacted with the acid?" The answer is "by the use of an indicator".

636. Indicators. Many indicators can be used in the reactions between an acid and an alkali, but they are not all equally useful. Those most commonly in use are litmus, methyl orange and phenolphthalein (see § 151).

Litmus can be used with what are termed "strong" acids, hydrochloric, nitric or sulphuric, in reactions with what are called "strong" alkalis, caustic soda and caustic potash, or with a "weak" alkali, sodium carbonate, if the solution is boiled.

Methyl orange can be used in the reactions between strong acids and strong alkalis and also in the reaction of strong acids with "weak" alkalis, such as ammonia, sodium carbonate and borax.

Phenolphthalein can be used in the reactions of any acid, the strong acids mentioned above and also "weak" acids such as acetic acid, oxalic acid and citric acid, with the strong alkalis, caustic soda and caustic potash.

Summarising the uses of the different indicators, we may say that for the reactions between

(i) a strong acid and a strong alkali, *any* indicator can be used;

(ii) a weak acid and a strong alkali, *phenolphthalein* should be used;

(iii) a strong acid and a weak alkali, *methyl orange* should be used.

For the reaction between a weak acid and a weak base no indicator is available, but such reactions are never necessary in volumetric analysis.

637. Apparatus. The special apparatus which is required for volumetric analysis consists of graduated cylinders, graduated flasks, pipettes and burettes (see fig. 86). It is important to notice the different purposes of each.

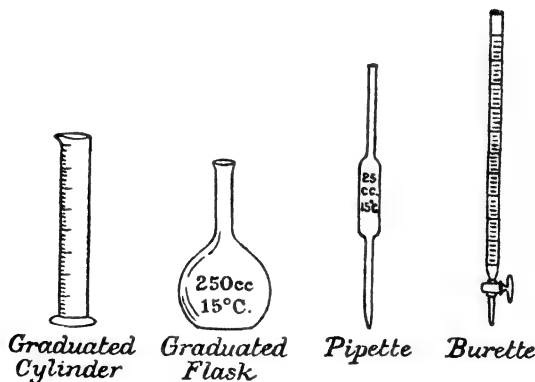


Fig. 86.

A graduated cylinder is marked to show the volume of liquid which it *contains* when filled up to one of its graduations. It is used for approximate work only.

A graduated flask has a mark on its neck; when filled to that

mark it *contains* the volume of liquid which is engraved on it; thus a flask marked 250 c.c. contains 250 c.c. of liquid when filled to the mark on the neck. A temperature (usually $15^{\circ}\text{C}.$) is also marked on the flask. This indicates that it contains the volume marked if the temperature is $15^{\circ}\text{C}.$; the liquid should be put into the flask at this temperature and not at any higher temperature.

Pipettes and burettes differ from graduated cylinders and flasks in that they *deliver* the volume of liquid which is marked on them.

When using a pipette care should be taken not to blow down the open end. If that is done, more liquid may be blown out than the pipette is intended to deliver. Pipettes are usually intended to leave a drop or two in the jet at the bottom. Certain pipettes marked "normal" are, however, intended to be emptied; in this case the last drops can be expelled by putting one finger on the top of the pipette and grasping the bulb with the other hand; the expansion of the air will expel the last drops. A pipette is filled with liquid by placing the lower end under the surface of the liquid and sucking with the mouth at the upper end. When the liquid has been drawn *above* the mark, the upper end is closed with the *first finger*, *not* with the thumb. The lower end is raised out of the liquid and the liquid in the pipette allowed to fall by slightly raising the finger on the upper end until it is level with the mark. The pipette should be held so that the mark is level with the eye and the liquid adjusted so that the *bottom* of its curved surfaces (or meniscus) is level with the mark (see fig. 87).

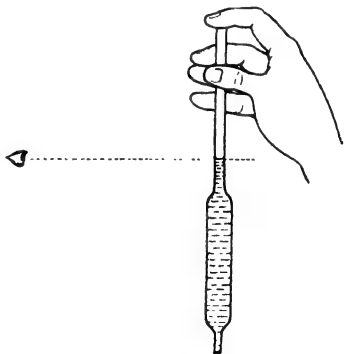


Fig. 87. Holding a pipette.

638. Before use in volumetric analysis the vessels (cylinders, flasks, pipettes and burettes) should be thoroughly cleaned with water (or, in cases where staining has occurred, with a suitable cleansing reagent) and then rinsed twice with a small quantity of distilled water. They should always be rinsed with a small quantity of the solution which is to be measured, the solution being brought into contact with all parts of the vessel by holding it nearly horizontal and rotating it in the hand.

639. There is one other point to which attention should be given when using a pipette: the lower end of the pipette should be *sufficiently below* the surface of the liquid before suction is applied at the upper end to ensure that no air is drawn with the pipette. It is usually safer to put the liquid in a beaker or flask of such a size that the pipette can touch the bottom. If this precaution is not taken the worker may easily get a mouthful of acid or alkali which is certain to be unpleasant and may be dangerous.

640. When using a burette it is important to see that the lower part, i.e. the tap and tube below the tap, is full of liquid. Some burettes have not glass taps but a piece of rubber tubing connected to a glass tube; these burettes are opened and closed by a clip or by a piece of glass rod in the rubber tubing. The lower part can be filled with liquid by turning it upwards and opening the clip or pulling the rubber tubing away from the glass rod. As with pipettes, it is important that the eye shall be level with the bottom of the meniscus and that the volume of the liquid shall always be recorded by the position of the bottom of the meniscus.

641. Method of titration. It is best to put the solution to be titrated in a conical flask rather than in a beaker. It will be found convenient to arrange the burette so that the tap is towards the right but to turn the tap with the left hand. In this way the risk of pulling out the tap can be diminished and also the right hand can be left free to shake the flask.

When titrating acids and alkalis it is best to put the alkali in the flask and the acid in the burette.

642. Time will be saved in titrations by making the first titration a rough one, running the solution from the burette 1 c.c. at a time. In this way the volume of solution required can be determined to an accuracy of about 1 c.c. In subsequent titrations nearly all the solution which must be run from the burette can be added at once. Suppose, for example, that in the first titration the colour of the indicator is unchanged after the addition of 23 c.c. but is changed after the addition of 24 c.c. In subsequent titrations 22 c.c. can be added at once and the titration finished drop by drop.

643. Entering results in the note-book. A little care taken in entering the results in the note-book will save time in the end. Suppose that 20 c.c. of a solution of caustic soda are to be titrated with $N/10$ oxalic acid solution; the results should be recorded as follows:

20 c.c. of caustic soda solution titrated with

	I	II	III	IV
Second reading	24.5	24.1	23.9	23.8
First reading	0.5	0.6	0.5	0.2
		23.5	23.4	23.6 c.c. <i>N</i> /10 oxalic acid.
Mean volume of <i>N</i> /10 oxalic acid = 23.5 c.c.				

STANDARD SOLUTIONS, NORMAL SOLUTIONS AND DECI-NORMAL SOLUTIONS

644. Standard solutions are solutions of known concentrations. Normal and deci-normal solutions are particular kinds of standard solutions (see also chap. xvi, § 161). A normal solution contains 1 gramme-equivalent of the dissolved substance in 1 litre. They are specially convenient because equal volumes of normal solutions will react together. For many purposes, solutions of one-tenth normal concentration (or deci-normal

solutions) will suffice. The amounts required for normal or deci-normal solutions can easily be calculated if the equivalent weight of the substance to be dissolved is known.

For example, the equivalent weight of caustic soda is 40; a litre of a normal or *N* solution of caustic soda will therefore contain 40 gm. of that compound and a litre of a deci-normal or *N/10* solution will contain 4 gm.

The following table of equivalent weights will be found useful.

Substance	Formula	Equivalent weight
Sulphuric acid	H_2SO_4	49
Hydrochloric acid	HCl	36.5
Nitric acid	HNO_3	63
Oxalic acid crystals	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	63
Oxalic acid anhydrous	$\text{H}_2\text{C}_2\text{O}_4$	45
Caustic soda	NaOH	40
Caustic potash	KOH	56
Sodium carbonate anhydrous	Na_2CO_3	53
Potassium permanganate	KMnO_4	31.6*

* (This is its equivalent considered as an oxidising agent in acid solution. See § 685.)

645. Preparation of standard solutions. In all volumetric work with acids and alkalis it is necessary to have one substance of great purity with which to prepare a solution of accurately known strength; the solutions of the other substances are standardised by comparison with it. If, for example, a solution of an acid can be prepared by weighing a quantity of the pure substance and dissolving it in water, the strength of a solution of an alkali can be determined by finding the volume of the alkaline solution which will neutralise a given volume of the acid solution.

Sulphuric acid, nitric acid, caustic soda, caustic potash are unsuitable for this purpose as they cannot be easily obtained in a state of purity and free from water. Standard solutions of these substances can only be prepared by indirect methods.

Various substances have been suggested as standards. One of these is sodium carbonate, another is oxalic acid (see § 156).

646. In preparing a standard solution of a solid substance, a quantity is weighed on a weighed watch-glass and then dissolved in distilled water. It is usually best to dissolve the solid in water in a beaker rather than in the graduated flask. After pouring the solid from the watch-glass into the beaker, the watch-glass should be washed with distilled water, the washings being poured into the beaker (see fig. 88). When the solid has all been dissolved, the solution is poured through a funnel into the graduated flask and the beaker is washed with distilled water, the washings being poured through the funnel into the graduated flask.

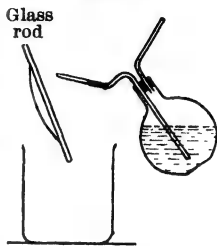


Fig. 88. Washing the watch-glass.

It is most important to remember to cork the flask and shake it thoroughly after it has been filled in order to mix the contents and ensure uniform concentration. *More mistakes in volumetric analysis are caused by neglect of thorough mixing than by any other means.*

EXPERIMENT 48. Preparation of a deci-normal solution of oxalic acid.

250 c.c. will suffice. As will be seen from the table in § 644 oxalic acid crystals have the formula $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and the equivalent weight is 63. 6.3 gm. will be required for a litre of $N/10$ solution and a quarter of this (or 1.575 gm.) for 250 c.c.

Weigh exactly 1.575 gm. of pure oxalic acid crystals on a weighed watch-glass; dissolve them in about 100 c.c. of distilled water in a beaker and then transfer the solution to a 250 c.c. flask. Rinse the beaker with distilled water, pouring the washings into the flask. Add more distilled water to make the solution up to the mark. Then cork the flask and shake it thoroughly.

EXPERIMENT 49. Preparation of a deci-normal solution of caustic soda.

As has already been mentioned, it is difficult to ensure that caustic soda does not contain some water or that it will not absorb moisture while it is being weighed. A solution which is certain to be somewhat stronger than deci-normal is therefore prepared and its strength is found by titration of measured portions with the deci-normal solution of oxalic acid already prepared.

A litre of deci-normal solution of caustic soda contains 4 gm. Weigh roughly 4.25 gm. on a watch-glass and dissolve it in 200 c.c. of distilled water in an ordinary flask. When it has all dissolved add 800 c.c. of distilled water. Cork the flask and shake thoroughly. Clean and rinse a 20 c.c. pipette, as instructed in § 638. Measure 20 c.c. of the caustic soda solution into a clean conical flask and add one or two drops of phenolphthalein solution.

Clean and rinse a burette (as instructed in § 638) with a little deci-normal oxalic acid solution and then fill it with the latter solution. Make sure that the lower part of the burette is filled with the solution. Record the level of the meniscus in the burette.

Run the oxalic acid into the caustic soda solution about 1 c.c. at a time until the colour of the phenolphthalein is discharged. Again record the level of the meniscus.

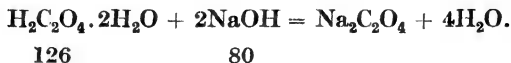
Empty the conical flask, wash it and rinse it with distilled water. Measure 20 c.c. of caustic soda solution and add phenolphthalein as before. Run in oxalic acid solution. This time nearly all the acid necessary can be added at one time; the titration can be finished one drop at a time, shaking the flask after each addition till the addition of one drop just discharges the colour of the phenolphthalein.

The titration must then be repeated at least twice. If the volumes of acid used do not differ by more than two-tenths of a

1 c.c. the mean of the last three titrations can be taken. We can now calculate the concentration of the caustic soda solution.

Suppose 23.5 c.c. of deci-normal oxalic acid solution neutralised 20 c.c. of caustic soda solution. The oxalic acid solution contains $\frac{23.5 \times 6.3}{1000}$ gm. of oxalic acid.

The equation is



That is to say

126 gm. of oxalic acid neutralise 80 gm. of caustic soda,

$\therefore \frac{23.5 \times 6.3}{1000}$ gm. of oxalic acid neutralise $\frac{80}{126} \times \frac{23.5 \times 6.3}{1000}$ or

0.094 gm. of caustic soda. That is to say 0.094 gm. of caustic soda is contained in 20 c.c. of the solution. If the solution was deci-normal, it would contain 4.0 gm. of caustic soda in a litre. 4.0 gm. of caustic soda are contained in

$$\frac{20 \times 4.0}{0.094}$$

or 851.0 c.c. of this solution. If 851.0 c.c. of this solution are taken and diluted to 1 litre, the solution will be deci-normal.

From your own observations you will have found that x c.c. of your solution contain 4.0 gm. of caustic soda. Clean and rinse with the caustic soda solution the necessary flasks, pipette and burette (say, 500 c.c., 250 c.c. flasks and a 50 c.c. pipette). Fill the flasks very carefully with the caustic soda solution and transfer their contents to a litre flask; rinse the flasks with distilled water, pouring the washings into the litre flask; add the remaining volumes of caustic soda solution by means of pipettes and finally with a burette. Then fill the litre flask to the mark with distilled water, cork it and shake thoroughly.

The concentration of the solution which you have made

should now be checked by titration with your deci-normal oxalic acid solution or with the laboratory $N/10$ sulphuric acid or $N/10$ hydrochloric acid. 20 c.c. of your caustic soda solution should require 20 c.c. of $N/10$ acid for neutralisation.

An ordinary flask or bottle should be cleaned and rinsed with the caustic soda solution. The rinsings having been poured into the sink, the solution can be transferred to this flask or bottle which should then be labelled $N/10$ caustic soda solution.

There is another method of calculating the volume of the solution of caustic soda which must be taken for dilution to 1 litre in order to prepare a deci-normal solution. Taking the hypothetical results given above, 20 c.c. of the caustic soda solution reacted with 23.5 c.c. of $N/10$ oxalic acid. If the caustic soda solution had been deci-normal, 20 c.c. of it would have reacted with 20 c.c. of $N/10$ oxalic acid solution. The caustic soda solution is therefore stronger than deci-normal and is in fact $23.5 \times \frac{N}{20 \times 10}$. If 20 c.c. of it are diluted to 23.5 c.c., the resulting solution will be deci-normal. To make 1000 c.c. of $N/10$ solution will require $\frac{1000 \times 20}{23.5}$ or 851.0 c.c. of the original caustic soda solution.

The former method is preferable as it takes account of the quantities required by the equation and can be used, with the necessary modification, with standard solutions which are not exactly normal or deci-normal.

EXPERIMENT 50. Preparation of deci-normal hydrochloric acid.

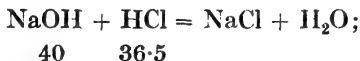
A deci-normal solution of hydrochloric acid can be prepared by passing dry gaseous hydrogen chloride into a weighed quantity of water and weighing the amount absorbed. The solution is then diluted to such a volume that the concentration is 3.65 gm. of hydrogen chloride per litre.

For use in a school laboratory a more rapid method is to dilute concentrated hydrochloric acid with water in such a proportion as to make a solution which is certain to be stronger than deci-normal and then to find the concentration by using it for the titration of measured portions of deci-normal caustic soda.

For this purpose 11 c.c. of concentrated hydrochloric acid are measured from a burette into a large flask and 1000 c.c. of distilled water are added from a measuring cylinder; the flask is then corked and thoroughly shaken. The concentration of this solution must now be found. Clean and rinse a burette with the solution and then fill it. Record the reading of the meniscus. Measure 20 c.c. of $N/10$ caustic soda solution into a conical flask, add one or two drops of phenolphthalein and then titrate the solution with the hydrochloric acid from the burette. Make the first titration a rough one (as described in § 642) and follow it by three careful titrations.

We must now find the concentration of the hydrochloric acid solution. The acid was made stronger than $N/10$ and the volumes of it required to neutralise 20 c.c. of $N/10$ caustic soda will be less than 20 c.c.; suppose the mean volume is 18.5 c.c.

The equation is



that is to say

40 gm. of caustic soda neutralise 36.5 gm. of hydrochloric acid.

20 c.c. of $N/10$ caustic soda solution contain $\frac{20 \times 4.0}{1000}$ or 0.08 gm. of caustic soda.

But 0.08 gm. of caustic soda will neutralise

$$\frac{36.5}{40} \times 0.08 \text{ or } 0.073 \text{ gm. of hydrochloric acid.}$$

This means that 0.073 gm. of hydrochloric acid is contained in

18.5 c.c. of the solution. If the solution was deci-normal, 3.65 gm. of hydrochloric acid would be contained in 1 litre, 3.65 gm. of the acid are contained in $\frac{3.65}{0.073} \times 18.5$ or 925.0 c.c. of this solution. If 925.0 c.c. of this solution are taken and diluted to 1 litre, the solution should be deci-normal.

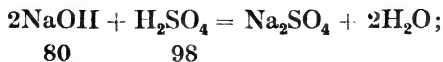
From your own observations you will have found that x c.c. of your solution contain 3.65 gm. of hydrochloric acid. Proceeding as before, measure x c.c. of your solution into a graduated litre flask and fill the flask to the mark with distilled water, cork it and shake it thoroughly. The concentration of the solution which you have made must now be checked by titration with your own or with the laboratory $N/10$ caustic soda solution. 20 c.c. of $N/10$ caustic soda solution should require 20 c.c. of your hydrochloric acid solution for neutralisation.

The solution should be transferred to an ordinary flask or bottle, taking the precautions mentioned in Exp. 49.

EXPERIMENT 51. Preparation of deci-normal sulphuric acid.

A similar method may be adopted for the preparation of deci-normal sulphuric acid. In this case, 200 c.c. of distilled water are put in a large flask; 3 c.c. of concentrated sulphuric acid are run in slowly from a burette. The flask is well shaken and 800 c.c. of distilled water are added from a measuring cylinder. The flask is corked and thoroughly shaken.

The solution will be stronger than $N/10$; its concentration is found in a similar manner to that described for hydrochloric acid. The equation is



that is to say 80 gm. of caustic soda react with 98 gm. of sulphuric acid.

The preparation of a deci-normal solution of hydrochloric

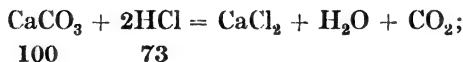
acid is preferable to that of sulphuric acid as it allows an independent check to be made either by titration with silver nitrate solution (which can be made by direct weighing) or by the following method.

EXPERIMENT 52. Another method of standardising the solution of hydrochloric acid.

The standardising substance employed in this method is Iceland spar, a very pure naturally occurring crystalline form of calcium carbonate.

Put some small compact fragments of Iceland spar in a dry beaker and weigh the beaker and its contents together. Measure into the beaker with a pipette 20 c.c. of your hydrochloric acid solution. Cover the beaker with a watch-glass and leave to stand for 24 hours. Boil to expel dissolved carbon dioxide from the solution, adding distilled water from time to time to prevent the solution from becoming too concentrated. Pour off the solution of calcium chloride from the excess of Iceland spar, which remains in the form of compact fragments. Wash the beaker and the Iceland spar several times with distilled water and dry (both together) at about 110° C. and then weigh again. The difference between the first and the last weights of the beaker and spar gives the weight of spar which has been dissolved in the 20 c.c. of hydrochloric acid solution taken.

The equation is:



that is to say, 100 gm. of calcium carbonate react with 73 gm. of hydrochloric acid.

Suppose that the loss of weight of the Iceland spar is 0.108 gm. By the equation 0.108 gm. of calcium carbonate reacts with

$$\frac{73}{100} \times 0.108 \text{ or } 0.079 \text{ gm. of hydrochloric acid.}$$

This means that 0.079 gm. of hydrochloric acid is contained in 20 c.c. of your hydrochloric acid. If the solution was deci-normal, 3.65 gm. of hydrochloric acid would be contained in 1 litre.

3.65 gm. of hydrochloric acid are contained in $\frac{3.65}{0.079} \times 20$ or 925 c.c. of your solution.

The dilution of the solution to deci-normal concentration can be carried out as described before.

EXPERIMENT 53. Preparation of deci-normal sodium carbonate solution.

Standard solutions of sodium carbonate can be prepared by direct weighing and can be used as a check on the solutions previously prepared.

Prepare some pure anhydrous sodium carbonate by heating about 3 gm. of pure sodium bicarbonate in a porcelain basin until no further loss of weight occurs:



After heating for about 15 min., allow the basin to cool in a desiccator and then weigh it. Heat it again for 10 min. and allow it to cool in a desiccator and weigh it. Repeat this process until the weight is constant. Then weigh exactly on a weighed watch-glass 1.325 gm. of the anhydrous carbonate. Dissolve this carefully in about 100 c.c. of water in a beaker; when it has all dissolved, transfer the solution into a 250 c.c. graduated flask and carefully rinse the beaker, pouring the washings into the flask. Fill the flask up to the mark with distilled water, cork it and shake thoroughly.

Test the sodium carbonate solution against your *N*/10 hydrochloric acid by titrating portions of 20 c.c. with the acid. In this case phenolphthalein cannot be used, as that indicator will be affected by the carbonic acid which is produced by some of the carbon dioxide remaining in solution:



There are two methods which can be adopted. An indicator can be used which is not sensitive to carbonic acid; such a one is methyl orange (see § 636). Or the solution can be boiled and the carbon dioxide expelled; in this case litmus may be used (see § 636). It is easier to use methyl orange.

If you use litmus, take 20 c.c. of the sodium carbonate solution in a conical flask, add two or three drops of litmus and run in $N/10$ acid from the burette until the litmus just goes red. Boil the solution to expel the carbon dioxide; the colour will change to blue again. Continue the titration until sufficient acid has been added to render the red colour permanent. The titration should be repeated with three further portions of 20 c.c., but in these cases nearly all the acid necessary can be added at once and the titration finished by adding a drop of acid at a time.

If the solutions agree together, 20 c.c. of the sodium carbonate solution will require exactly 20 c.c. of $N/10$ acid.

647. Examples of the use of normal and deci-normal solutions.

EXPERIMENT 54. Determination of the percentage of water of crystallisation in washing soda.

Washing soda is a crystalline compound of sodium carbonate and water, and may be regarded for our purpose as $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$; the problem is to find x .

Choose some clear (not white) pieces of washing soda and put them in a weighing bottle (do not use a watch-glass, as washing soda is efflorescent). Weigh the bottle carefully. Pour about 4 gm. of the solid into a dry beaker; close the bottle and weigh again. The difference between the weights is the amount of washing soda you have taken. Dissolve the washing soda in about 100 c.c. of distilled water and transfer the solution to a 250 c.c. graduated flask and fill it up to the mark. Shake thoroughly to ensure uniform concentration.

Titrate portions of 20 c.c. with $N/10$ HCl solution, using methyl orange as an indicator (see Exp. 53).

You know that 1 litre of $N/10$ HCl solution will react with 53 gm. of anhydrous sodium carbonate (53 is the equivalent weight, see § 644). Hence calculate the weight of anhydrous sodium carbonate in the weight of washing soda which you used. Then calculate the weight of water which would be combined with 106 gm. of sodium carbonate (i.e. its molecular weight in grammes). From this the number of molecules of water combined with one molecule of Na_2CO_3 can be calculated.

EXPERIMENT 55. Determination of the equivalent weight of a metal.

This is a useful example of the method of "back titration".

In this case a *normal* solution of an acid is required; if a deci-normal solution is used, either a very small quantity of the metal must be used (when accurate weighing will be difficult) or large quantities of acid must be used.

Weigh accurately about 0.3 gm. of clean magnesium ribbon (or 0.8 gm. of clean zinc foil) and place it in a small flask. Add from a pipette 40 c.c. of N HCl solution (or N H_2SO_4 solution). When the action has ceased, titrate the solution with normal caustic soda solution, using any indicator.

Remembering that 1 c.c. of N caustic soda solution will react with 1 c.c. of N HCl solution, find by subtraction the volume of N HCl solution which would have just dissolved the weight of magnesium (or zinc) which you used. Hence calculate the weight of metal which 1 litre of N HCl solution would just dissolve. Since 1 litre of a normal solution of HCl contains 1 gramme-equivalent weight of HCl, this weight of metal must be its gramme-equivalent weight.

EXPERIMENT 56. Determination of the percentage of ammonia in ammonium sulphate.

Weigh accurately about 1.5 gm. of ammonium sulphate on a

weighed watch-glass. Dissolve the solid in distilled water in a beaker. Transfer the solution to a 250 c.c. graduated flask; fill the flask up to the mark and shake thoroughly. Measure 20 c.c. of this solution into a conical flask and add 40 c.c. of *N*/10 caustic soda solution. Ammonium sulphate and caustic soda react in accordance with the equation



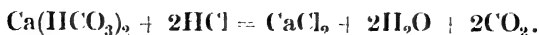
Boil the solution to expel the ammonia; when no more ammonia can be detected in the escaping steam by means of red litmus paper or turmeric paper, titrate the remaining liquid with *N*/10 HCl solution or *N*/10 H_2SO_4 solution. This first titration may be a rough one; it should be followed by careful titrations of three other portions of 20 c.c. treated in the same manner.

Find by subtraction the volume of *N*/10 caustic soda solution which would have just decomposed the ammonium sulphate in the 20 c.c. of the solution. Remembering that 40 gm. of caustic soda liberate 17 gm. of ammonia from ammonium sulphate, calculate the weight of ammonia in the ammonium sulphate which you took and hence the percentage of ammonia in ammonium sulphate.

This method could be used to find the percentage of an ammonium salt in a mixture of that salt with other compounds provided that those other compounds do not react with caustic soda. It could not be used to find the percentage of ammonia in a salt such as ferrous ammonium sulphate or ferric ammonium alum, as the iron sulphates react with caustic soda.

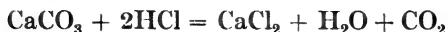
EXPERIMENT 57. Determination of the temporary hardness of water.

As is explained in § 233 the temporary hardness of water is due to the presence of calcium and magnesium bicarbonates. These bicarbonates react with hydrochloric acid in accordance with the equation



The result of titrating a quantity of hard water with $N/10$ HCl will be to give us the quantity of hydrochloric acid with which the water has reacted. So far as the consumption of acid is concerned, this is the same as that which would have been used if the calcium and magnesium bicarbonates had been replaced by calcium carbonate.

Compare the equation



with that given above. The hardness is therefore expressed in terms of parts of calcium carbonate per 100,000 of water. There is a further advantage in this method: it will be seen from the equation that 73 gm. of HCl react with 100 gm. of calcium carbonate; therefore 2 litres of N HCl react with 100 gm. of calcium carbonate or 200 c.c. of $N/10$ HCl with 1 gm. of calcium carbonate. This simplifies the arithmetic involved.

Measure 250 or 500 c.c. of hard water into an ordinary flask of about a litre capacity. Add just enough methyl orange to give a *faint* yellow colour; and titrate with $N/10$ HCl solution. Calculate the volume of $N/10$ HCl solution which would react with 100 litres of hard water and from this the weight of calcium carbonate per 100 litres.

648. Exercises in titrations of acids and alkalis.

(1) Find the equivalent weight of potassium bicarbonate (potassium hydrogen carbonate).

Weigh accurately about 2.5 gm.; dissolve in water and make up to 250 c.c. in a graduated flask. Titrate portions with $N/10$ HCl, using methyl orange as an indicator.

(2) Find the equivalent weight of calcium carbonate.

Weigh accurately about 1 gm.; dissolve in 40 c.c. N HCl and estimate excess of acid with N NaOH (see § 636 for indicator).

(3) Find the weight of magnesium oxide which will react with 36.5 gm. of hydrochloric acid.

Make an approximately normal solution of HCl by diluting 25 c.c. of concentrated acid to 250 c.c. Weigh accurately about 1.5 gm. of MgO and dissolve in 100 c.c. of the HCl solution; dilute to 250 c.c. in a graduated flask. Titrate portions of 20 c.c. of the solution with $N/10$ NaOH.

Measure with a pipette 10 c.c. of the approximately normal solution of hydrochloric acid and dilute to 100 c.c. in a graduated flask. Titrate portions of this solution with $N/10$ NaOH.

Calculate the weight of hydrochloric acid in 100 c.c. of the original acid solution; then find the amount of hydrochloric acid in 100 c.c. of the solution after the magnesium oxide has dissolved. Hence calculate the weight of magnesium oxide which will react with 36.5 gm. of hydrochloric acid.

(4) Find the equivalent weight of citric acid.

Weigh accurately about 1 gm., dissolve in water and make up to 100 c.c. in a graduated flask. Titrate portions of 20 c.c. with a standard solution of caustic soda of approximately normal concentration, using phenolphthalein as an indicator.

(5) Find the concentration of a solution of sodium carbonate of approximately $N/10$ concentration by means of potassium bisulphate.

Weigh accurately about 1.4 gm. of potassium bisulphate, dissolve in water and dilute to 100 c.c. in a graduated flask. Titrate portions of 20 c.c. of the sodium carbonate solution with the solution of potassium bisulphate, using methyl orange as an indicator.

Use the equation which follows:



(C = 12, O = 16, Na = 23, S = 32, K = 39.)

Chapter XLVII

THE HALOGENS

649. Precautions. Before describing the preparation of these elements and their compounds it is desirable to caution the student against inhaling any of them. *The preparation and collection should always be carried out in a fume cupboard.* But there will certainly be many occasions when the halogens will be produced in the laboratory, although they are not being deliberately prepared and collected. For example, it is often necessary when testing for chlorides to perform experiments which may produce one of the halogens. In such cases, use the smallest possible quantity of the substance and do not hold the test-tube near the nose. Empty the tube into the sink as soon as possible and run plenty of water down it.

If by mischance a small quantity of the gas is inhaled, relief can be obtained by *careful* inhaling of ammonia and by gargling with a solution of sodium bicarbonate.

CHLORINE

650. Preparation.

EXPERIMENT 58. The easiest method is by the action of concentrated hydrochloric acid on potassium permanganate (fig. 89); 5 gm. of the solid will yield about 1000 c.c. of the gas. Small jars of about 50 c.c. capacity will suffice for all the tests except (2), where a jar of about 200 c.c. is desirable. Heat is not necessary. Chlorine is very poisonous and must be prepared in a fume cupboard.

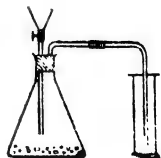


Fig. 89. Preparation of Chlorine.

Collect it by displacement of air (it is soluble in water), passing the gas to the bottom of a jar standing with its mouth upwards. Dry it (if necessary) by passage through a U-tube or tower containing small lumps of calcium chloride or through a bottle containing concentrated sulphuric acid (fig. 90).

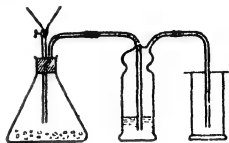


Fig. 90. Drying of Chlorine.

Properties. Examine it as follows, being very careful not to inhale any of it.

(1) Insert a burning taper. Note the character of the smoke; test it with a piece of damp blue litmus paper.

(2) Burn hydrogen in it (see fig. 91). Test the gas produced with damp blue litmus paper.

(3) Boil a *little* turpentine in an evaporating basin (be careful, use a small flame). When the turpentine is boiling, put out the flame, dip a narrow strip of filter paper in it and put the paper quickly into a jar of the gas. Note the result. Test the gas with damp blue litmus paper.

(4) Put a small piece of yellow phosphorus in a cold dry deflagrating spoon and insert it in a jar of the gas.

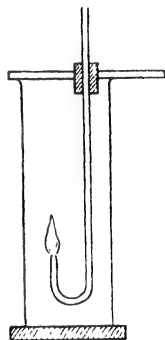
(5) Drop some finely powdered antimony into the gas.

(6) Invert a jar of the gas in water in a pneumatic trough and observe what happens.

(7) Invert a jar of the gas in a solution of caustic soda in a porcelain basin.

(8) Fill a gas jar with sulphuretted hydrogen gas; place this over a jar of chlorine and withdraw the plates.

(9) Insert into a jar a piece of starch paper which has been



Jet of Hydrogen or Coal Gas burning in Chlorine

Fig. 91.

dipped in a solution of potassium iodide. Note the colour, which is due to the liberation of iodine by the chlorine:



(10) Test the bleaching action of chlorine with (a) a damp, coloured flower, (b) a damp strip of paper with some writing on it, (c) a damp strip of printed paper, (d) a damp strip of turkey red twill.

651. Other methods of preparation.

Chlorine can also be prepared by (a) heating manganese dioxide with concentrated hydrochloric acid (see fig. 92), or (b) by heating a mixture of manganese dioxide and a chloride (usually common salt) with concentrated sulphuric acid, or (c) by heating bleaching powder with dilute sulphuric acid.

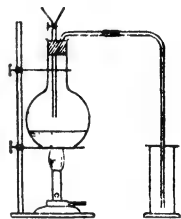


Fig. 92. Preparation of Chlorine from Manganese Dioxide.

BROMINE

652. Preparation. Bromine can be prepared by heating manganese dioxide and potassium bromide with concentrated sulphuric acid. This is best carried out in a retort, the bromine being condensed in a flask cooled with water.

Properties. As bromine is a liquid at ordinary temperatures, it is more easily transported than chlorine and can be sold and stored in ordinary bottles. It is therefore not necessary to prepare the element yourself in order to examine its properties.

EXPERIMENT 59. Examine bromine as follows, remembering that it is very poisonous:

(1) Shake a few drops with 10 c.c. of water in a test-tube and notice the colour of the liquid produced.

(2) Dip in the solution just made a piece of starch paper which has been soaked in potassium iodide solution. Notice the colour produced.

(3) Test its bleaching action by putting in the solution a coloured flower, and a piece of paper with writing on it.

(4) Warm a few drops of bromine in a wide test-tube and insert a burning taper.

(5) Warm a few drops of bromine in a wide test-tube and drop into it a little finely powdered antimony.

(6) Shake about 5 c.c. of bromine solution with 1 c.c. of carbon disulphide—note the colour produced in the carbon disulphide.

IODINE

653. Preparation. Iodine can be prepared by heating manganese dioxide and potassium iodide with concentrated sulphuric acid in a retort. The iodine sublimes into the neck of the retort and the flask (see fig. 34).

Properties. It is not necessary to prepare iodine in the laboratory in order to examine its properties; it is a solid at ordinary temperatures, is easily transportable and can be purchased in the ordinary way.

EXPERIMENT 60. Examine some iodine as follows:

(1) Warm a few fragments in a dry test-tube. Note the colour of the vapour and also the formation of crystals in the upper (cooler) parts of the tube.

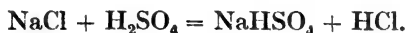
(2) Grind a little starch with water in a mortar and pour the thin paste into a beaker of boiling water. Shake some small fragments of iodine with water and add a few drops of the starch solution. Note the colour produced.

(3) Test the solubility of iodine in the following, using only about 1 c.c. of liquid in each case: (a) potassium iodide solution, (b) industrial spirit (alcohol), (c) benzene, (d) carbon disulphide, (e) chloroform.

HYDROGEN CHLORIDE OR HYDROCHLORIC ACID GAS

654. Preparation.

EXPERIMENT 61. The gas is prepared by the action of concentrated sulphuric acid on common salt; 3 gm. of the solid will yield about 1000 c.c. of gas. The apparatus is the same as that used for preparing chlorine (fig. 92); the reaction begins in the cold but heat is required to finish it. The equation for the reaction in the laboratory is



The second equation in § 192 requires a much higher temperature than is employed in a school laboratory.

Collect the gas by displacement of air (it is very soluble in water), passing the gas to the bottom of a jar standing with its mouth upwards. Cover the jar with a piece of perforated cardboard. Dry the gas (if necessary) by passing it through a bottle containing concentrated sulphuric acid or a tower or U-tube of calcium chloride. You will require 5 jars of about 50 c.c. capacity; you should be ready to carry out tests (7), (8) and (9) before you begin collecting the gas.

Properties. As you collect observe that it is colourless, it fumes in moist air (especially if you blow across the top of a jar) and has a choking smell. Examine jars of it as follows:

(1) Insert a burning taper—does the gas burn or support combustion?

(2) Insert burning phosphorus on a deflagrating spoon.

(3) Invert a jar in water. Remove the jar with the water it contains and test it with litmus and other indicators.

(4) Invert a jar in caustic soda solution.

(5) Put a few drops of 0.880 ammonia solution in a gas jar, cover it with a glass plate and shake thoroughly. Draw the

plate slightly aside and let the liquid run out. Replace the plate and invert over it a jar of hydrogen chloride. Withdraw the plates.

(6) Add to some of the solution a few drops of silver nitrate solution. Notice the white precipitate; see whether it is dissolved by adding a few drops of dilute nitric acid.

Carry out the following tests with the gas as it comes from the generating flask:

(7) Pass the gas through a heated tube containing manganese dioxide and test the issuing gas with a piece of starch paper which has been dipped in a solution of potassium iodide.

(8) Pass the gas through a heated tube containing magnesium filings and collect the resulting gas over water. Test it with a taper (see fig. 93).

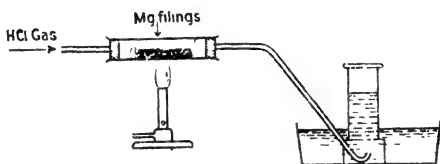


Fig. 93. Action of Magnesium on Hydrogen Chloride.

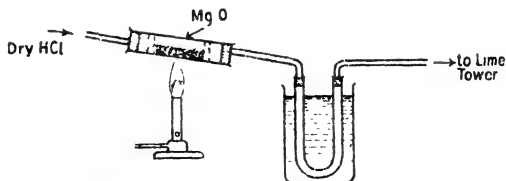


Fig. 94. Action of Magnesium Oxide on Hydrogen Chloride.

(9) Pass the *dried* gas through a heated tube containing magnesium oxide and condense the resulting vapour in a cooled U-tube (see fig. 94).

Test (8) produces a white solid and hydrogen; test (9) produces a white solid and water:

Hydrogen chloride + magnesium produce
magnesium chloride + hydrogen.

Hydrogen chloride + magnesium oxide produce
magnesium chloride + water.

You have already shown (Exps. 16 and 35) that hydrochloric acid solution evolves hydrogen when magnesium, zinc, iron or aluminium is added to it and that it produces carbon dioxide with sodium carbonate, iodine with a mixture of potassium iodide and iodate, sulphuretted hydrogen with sodium sulphide.

The reactions by which chlorides can be detected or identified are given in § 692.

HYPOCHLOROUS ACID AND HYPOCHLORITES

655. Preparation and Properties.

EXPERIMENT 62. A mixture of sodium hypochlorite and sodium chloride in solution can be prepared by passing chlorine into cold dilute caustic soda solution (see § 209).

The liquid obtained by grinding a little bleaching powder with water in a mortar is a similar solution of calcium hypochlorite and calcium chloride. Either of these will show the characteristic properties of hypochlorites. Examine them as follows:

(1) Add about half of 1 c.c. of dilute hydrochloric acid; prove that chlorine is evolved.

(2) Dip a piece of coloured cloth in the solution, withdraw it and dip it in dilute sulphuric acid.

(3) Mix a few c.c. of the solution with about an equal volume of 5 per cent. solution of manganese chloride, add 1 c.c. of caustic soda solution and boil.

Observe that a brown precipitate of hydrated manganese *dioxide* is obtained; this shows that the hypochlorite is an oxidising agent.

(4) Oxygen can be prepared from bleaching powder by the catalytic action of cobalt hydroxide.

Grind a few grammes of bleaching powder in a mortar with a little water to form a thin cream. Put the creamy liquid into a small flask and arrange as shown in figs. 97 or 103. Run in a few c.c. of cobalt chloride solution through the funnel and then warm the flask. The cobalt chloride reacts with the calcium hydroxide in the bleaching powder to form cobalt hydroxide, which acts upon the warm bleaching powder liberating oxygen.

CHLORATES

656. Preparation and properties. A mixture of potassium chloride and chlorate can be prepared by passing chlorine into a hot strong solution of caustic potash; the two substances can be separated by crystallisation (see §§ 94 and 209).

EXPERIMENT 63. Examine some potassium chlorate as follows:

(1) Heat a little in a hard glass tube and prove that oxygen is given off. When no more gas is evolved, allow the residue to cool. Remove a portion about the size of a small pea and warm it in a test-tube with an equal amount of manganese dioxide and half of 1 c.c. of concentrated sulphuric acid. Prove that chlorine is evolved.

Dissolve another small portion of the residue in distilled water, add half of 1 c.c. of dilute nitric acid and 1 c.c. of silver nitrate solution.

These tests prove that when a chlorate is heated, a chloride is left.

(2) Add 1 c.c. of concentrated hydrochloric acid to a small piece of potassium chlorate and warm gently. Note the colour of the liquid and the gas. Smell it *very cautiously*. It is a mixture of chlorine and chlorine peroxide, sometimes called "euchlorine".

Chapter XLVIII

OXIDES OF CARBON

CARBON DIOXIDE

657. Preparation.

EXPERIMENT 64. The easiest method of preparation consists in running concentrated hydrochloric acid on to fragments of marble which have been covered with a layer of water. No heat is required (see fig. 95). Collect the gas by displacement of air (it is soluble in water and heavier than air) by passing it to the bottom of a jar standing with its mouth upwards. 5 gm. of marble and 10 c.c. of concentrated hydrochloric acid (diluted as above) will yield about 1000 c.c. of the gas. Five small jars of 50 c.c. capacity and one of 300 c.c. are required.

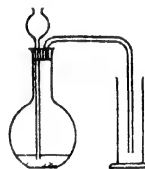


Fig. 95. Preparation of Carbon Dioxide.

Properties. Examine the gas as follows:

- (1) Smell it.
- (2) Insert a burning taper.
- (3) Take a jar containing about 300 c.c. of the gas and plunge in it a deflagrating spoon to which is attached a piece of burning magnesium ribbon. Notice what is produced.
- (4) Invert a small jar in water. Let it stand.
- (5) Pour about 2 c.c. of litmus solution into a small jar of the gas and shake. Observe the peculiar colour.
- (6) Invert a small jar in a basin containing caustic soda solution.
- (7) Bubble the gas through lime water (take about half a test-tube full). Continue passing the gas until the liquid becomes

clear again. Divide the clear liquid into two portions; to one add an equal quantity of lime water; boil the other. Describe and explain what happens and write the equations.

Other methods of preparation. Carbon dioxide can also be prepared by the action of very many acids on carbonates.

It is well to remember its formation (*a*) by burning carbon, and (*b*) by heating calcium carbonate.

658. Volumetric composition of carbon dioxide. An interesting method of proving that the volume of carbon dioxide produced when carbon burns in oxygen is equal to the volume of oxygen is the following*:

EXPERIMENT 65. A pyrex tube *A* (fig. 96) is fitted with a cork carrying two tubes, one of which passes to the end of *A* and has its other end closed with a rubber tube and clip; the second tube only just passes through the cork and is connected to a manometer tube *EFGK* containing mercury. A piece of carbon about the size of a pea is placed in *A* and the cork *loosely* inserted. Dry oxygen is passed through *CD* till the air has been displaced. The clip being open, the cork is pressed in. The clip is then closed. The levels of the mercury in the two limbs of the manometer should be the same. *A* is carefully warmed at first and then the carbon is heated till it catches fire. It is allowed to burn and then to cool. The levels of the mercury in the two limbs of the manometer tube will be found to be the same, showing that the volume of carbon dioxide formed is the same as that of the oxygen used. A molecule of carbon dioxide is therefore formed from a molecule of oxygen.

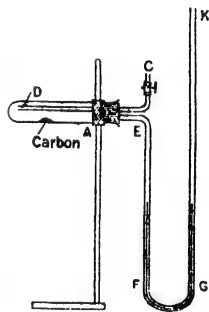


Fig. 96. Composition of Carbon Dioxide.

* This method is described by F. Fairbrother in the *School Science Review* and in the *Science Master's Book*.

CARBON MONOXIDE

659. Precautions. This is a very poisonous gas; it has very little smell and no colour, and does not give any warning of its presence. A small quantity will render anyone unconscious, in which state the unfortunate victim may easily inhale a fatal dose. The preparation should be carried out in a fume cupboard and great care should be taken not to inhale the gas.

Preparation. There are two easy methods of preparation.

EXPERIMENT 66. (a) From formic acid or sodium formate by heating with concentrated sulphuric acid. The formic acid or sodium formate is placed in the flask (see fig. 97); and the sulphuric acid is run down the funnel and the flask is gently heated.

0.6 gm. of formic acid or 1 gm. of sodium formate will yield about 250 c.c. of the gas.

(b) From oxalic acid by treating with concentrated sulphuric acid. In this case equal volumes of carbon monoxide and carbon dioxide are produced; as the carbon monoxide alone is wanted, the carbon dioxide is absorbed by passage through a bottle containing caustic soda solution (see fig. 98). Otherwise the preparation is the same as in (a). 1.5 gm. of oxalic acid will yield about 250 c.c. of the gas. Only 2 small jars of 50 c.c. are required for tests (1) and (2).

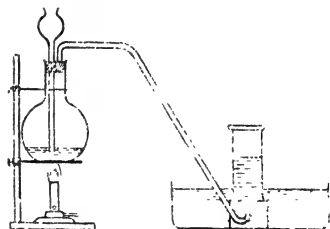


Fig. 97. Preparation of Carbon Monoxide from Formic Acid.

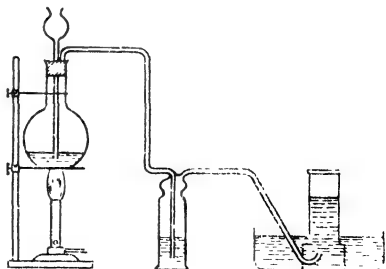


Fig. 98. Preparation of Carbon Monoxide from Oxalic Acid.

Properties. Examine the gas as follows (do not attempt to smell it):

(1) Apply a taper to a small jar. Note the colour of the flame. After the flame has gone out, add a few drops of lime water, replace the plate and shake. If the gas has been prepared from oxalic acid, it will be necessary to make sure that the gas you collected was completely freed from carbon dioxide.

(2) Invert a small jar in a dish containing an ammoniacal solution of cuprous chloride.

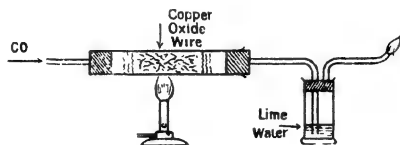


Fig. 99. Reduction of Copper Oxide by Carbon Monoxide.

(3) (This experiment should only be performed under the guidance of a teacher.) Pass the gas through a tube containing copper oxide (see fig. 99). When the air has been displaced, light the issuing gas and then heat the copper oxide. What happens to the copper oxide and what gas is produced?

Chapter XLIX

AMMONIA

660. Preparation.

EXPERIMENT 67. Ammonia can be prepared by heating in a round-bottomed flask a mixture of ammonium chloride or sulphate and slaked lime with sufficient water to make a thick liquid. The water is added to prevent the flask cracking. 2.5 gm. of the chloride or 3 gm. of the sulphate mixed with an equal weight of quicklime will yield 1000 c.c. of the gas. The flask must be heated. If the gas is required dry, it must be passed through a tower containing quicklime (see § 286). Collect it by displacement of air (it is very soluble in water and is lighter than air), passing it to the top of a dry jar supported with its mouth downwards (fig. 100). When a piece of damp red litmus held at the mouth of the jar is turned blue, remove the jar, close it with a plate and stand it on the bench, mouth downwards.

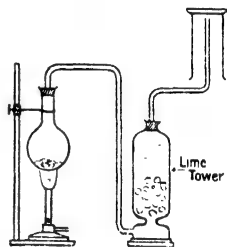


Fig. 100. Preparation of Ammonia.

Properties. The gas is obviously colourless and has a characteristic smell. Examine it as follows:

- (1) Insert a burning taper.
- (2) Invert a jar in water and remove the plate. Remove the jar with the water in it and test it with red litmus paper.
- (3) Take an empty jar and put in a few c.c. of concentrated hydrochloric acid. Cover it with a plate and shake it. Draw the plate slightly to one side and let the liquid run out into the sink. Close the jar at once and invert over it a jar of ammonia; remove the two plates. The white solid formed is a compound of ammonia and hydrochloric acid.

(4) Pass dry ammonia over heated copper oxide (see fig. 101). Condense the water that is formed in a U-tube and collect the gas in small jars over water. Examine it with (a) a taper, (b) lime water. What has happened to the copper oxide?

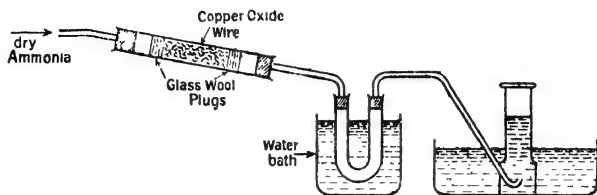


Fig. 101. Action of Ammonia on Copper Oxide.

Carry out the following tests with a solution of ammonia:

(5) Add a few drops of the solution to about 5 c.c. of copper sulphate solution. Note what happens. Add more ammonia solution until the liquid becomes clear again. Note the colour.

(6) Add a drop of ammonia solution to 10 c.c. of water, shake and then add 2 drops of Nessler's solution. Note what happens. Repeat this with a much more dilute solution of ammonia. Nessler's solution is obviously a very sensitive reagent for ammonia.

(7) Repeat (6) with dilute solutions of any ammonium compound.

[Nessler's solution is an alkaline solution of a double iodide of potassium and mercury (see § 288).]

661. Other methods of preparation. Ammonia can also be prepared by heating any ammonium compound with slaked lime or with a solution of caustic soda or caustic potash. These reactions can be carried out in test-tubes, using very small quantities and testing the gas by its smell, its action on damp red litmus paper, or by holding in the mouth of the tube a strip of filter paper which has been dipped in Nessler's solution.

Chapter L

ACIDS AND OXIDES OF NITROGEN

NITRIC ACID

662. It is not necessary to prepare nitric acid in the laboratory in order to study its properties.

EXPERIMENT 68. Properties.

(1) Note its colour and that it is heavy and oily.

(2) As is stated in chap. XXII, § 294, nitric acid is a powerful oxidising agent; this can be demonstrated by heating some sawdust on an iron plate and when it is hot dropping on it a few drops of concentrated nitric acid. The burning of the sawdust is due to the oxygen in the nitric acid.

(3) Warm a small quantity of flowers of sulphur with 3 or 4 c.c. of concentrated nitric acid for 4 or 5 min. Allow the unchanged sulphur to settle and pour off the clear liquid into another test-tube. Add about an equal quantity of distilled water and a few drops of barium chloride solution. The white precipitate which is produced is evidence of the formation of sulphuric acid by oxidation of sulphur.

(4) Add a few c.c. of concentrated nitric acid to some copper turnings in a test-tube; warm if necessary. Do not smell the gas evolved; it is poisonous. Repeat with iron, zinc, tin and lead. You have already carried out (see Exp. 35) a number of tests with dilute nitric acid which are common to the majority of acids.

663. Nitrates.

EXPERIMENT 69. Test some sodium nitrate or potassium nitrate in the following ways:

(1) Warm a small quantity in a test-tube with a few c.c. of concentrated sulphuric acid.

(2) Warm a small quantity of the nitrate with some copper turnings and a few c.c. of concentrated sulphuric acid.

(3) Dissolve a small quantity of ferrous sulphate in 5 c.c. of distilled water; add a small crystal of the nitrate and cool the solution if necessary. Incline the test-tube and pour down the side of the tube 2 or 3 c.c. of concentrated sulphuric acid. The acid will form a separate layer at the bottom of the tube; where it meets the solution of ferrous sulphate and the nitrate, a brown ring is formed. This is the *brown ring test*.

664. Action of heat on nitrates. Nitrates do not all behave in the same way when heated. The differences should be noted.

EXPERIMENT 70. Heat in small hard-glass test-tubes:

(a) Some potassium nitrate; test the gas evolved with a glowing splinter of wood.

(b) Some sodium nitrate and test in the same way.

(c) Some lead nitrate.

(d) The nitrate of any other metal.

665. Nitrites.

EXPERIMENT 71. Test some sodium or potassium nitrite as follows:

(1) Add 2 or 3 c.c. of *dilute* sulphuric acid to a few crystals of the nitrite and warm gently.

(2) Dissolve a small quantity of ferrous sulphate in distilled water and add a small quantity of a solution of the nitrite and about 1 c.c. of *dilute* sulphuric acid. Warm the liquid, carefully observing the gas which is evolved (see also Exp. 72(b)).

OXIDES OF NITROGEN

666. The two oxides which can easily be prepared in the laboratory are nitrous oxide N_2O and nitric oxide NO . It is more convenient to prepare nitric oxide first, as a little of it is to be used in an experiment with nitrous oxide.

667. Nitric oxide.**EXPERIMENT 72. Preparation.**

(a) The usual method of preparation consists in acting on dilute nitric acid with copper. It is important to notice that the acid *must be dilute*; if concentrated acid is used, no nitric oxide will be obtained. The apparatus is shown in fig. 102; the copper is placed in the flask and covered with a layer of water; concentrated nitric acid is poured down the funnel. A vigorous action occurs; brown fumes are formed but these disappear as the air is expelled. When the gas in the flask becomes colourless, it

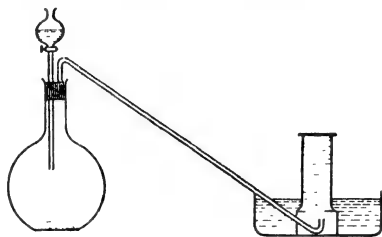
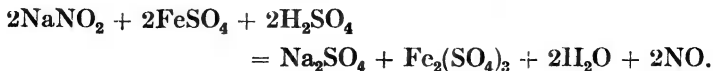


Fig. 102. Preparation of Nitric Oxide.

can be collected in jars over water. Heat is not necessary. 5 gm. of copper and 11 c.c. of concentrated nitric acid mixed with an equal volume of water will yield rather less than 1 litre of gas.

(b) An easier method of preparation which yields pure nitric oxide consists in boiling a mixture of the solutions of sodium nitrite, ferrous sulphate and sulphuric acid:



3 gm. of sodium nitrite, 12 gm. of crystals of ferrous sulphate and 4 c.c. of sulphuric acid will yield 1000 c.c. of gas.

The sodium nitrite is dissolved in 20 c.c. of water in a small flask, and the ferrous sulphate is dissolved in about an equal

volume of water, the sulphuric acid is added to it and the solution is then run in a little at a time through the funnel. The liquid is heated and may finally be boiled (fig. 103).

Properties. The gas is obviously colourless and insoluble in water. Examine it as follows:

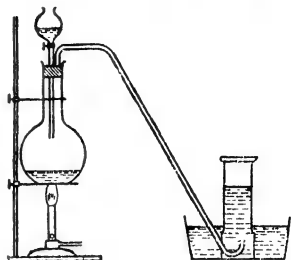


Fig. 108. Preparation of Nitric Oxide.

(1) Invert a jar over a beehive shelf in water and bubble in a *little* oxygen. Notice the formation of brown fumes and observe that they dissolve in water. Careful addition of oxygen would cause the jar to fill with water, if the nitric oxide was pure.

(2) Remove the plate from a jar. Observe the brown fumes. [Note: these fumes are poisonous.] As the gas forms brown fumes with air, its taste and smell cannot be detected. The formation of these fumes with air proves that air contains free or uncombined oxygen.

(3) Insert a burning taper.

(4) Insert a deflagrating spoon with vigorously burning phosphorus.

(5) Repeat with phosphorus just alight.

(6) Repeat with sulphur.

(7) Add a few c.c. of ferrous sulphate solution to a jar of the gas, and shake.

(8) Add 1 c.c. of carbon disulphide (be careful, as this compound is very inflammable) to a jar of the gas; quickly replace the plate, and shake. Remove the plate and without bringing your head near the jar immediately apply a lighted taper.

668. Other methods of preparation. (a) By heating mercury with sodium nitrate and concentrated sulphuric acid.

(b) By adding cold concentrated sulphuric acid to solid potassium nitrate (or sodium nitrate) and then pouring in a saturated solution of ferrous sulphate. On mixing the liquids, heat is evolved and nitric oxide set free (see § 298).

669. Nitrous oxide.

EXPERIMENT 73. Preparation.

The usual method of preparation consists in heating ammonium nitrate. There is always a risk of an explosion, if the heating is not carefully controlled. It is safer to heat a mixture of potassium nitrate (or sodium nitrate) and ammonium sulphate. In either case it is wise to stop heating before all the ammonium nitrate has decomposed. 4 gm. of sodium nitrate (or 5 of potassium nitrate) and 3 gm. of ammonium sulphate will yield 1000 c.c.

The gas is moderately soluble in cold water but much less in hot water (see § 296), and is usually collected over the latter (see fig. 104).

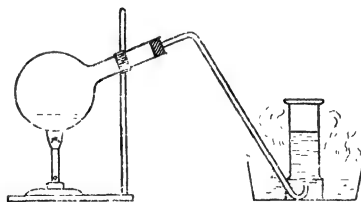


Fig. 104. Preparation of Nitrous Oxide.

Properties. Examine the gas as follows:

- (1) Insert a glowing splinter.
- (2) Insert a deflagrating spoon with burning phosphorus.
- (3) and (4) Repeat with sulphur and carbon.

(5) Invert a jar of *nitric* oxide over a beehive shelf in water and bubble a little *nitrous* oxide into it.

(6) Invert a jar in an alkaline solution of pyrogallol.

670. Distinguishing nitrous oxide from oxygen.

Nitrous oxide obviously resembles oxygen in rekindling a glowing splinter. Nitrous oxide differs from oxygen in (*a*) smell, (*b*) solubility in water, (*c*) not forming brown fumes with nitric oxide, (*d*) not being absorbed by an alkaline solution of pyrogallol.

Chapter LI

COMPOUNDS OF SULPHUR

SULPHUR DIOXIDE

671. Preparation and properties.

The gas is poisonous and must be prepared in the fume cupboard.

EXPERIMENT 74. The commercial process consists in burning sulphur or iron pyrites in a current of air. The gas obtained obviously contains 79 per cent. of nitrogen. This method of preparation can be repeated in the laboratory fume cupboard (see fig. 105). Air is blown out of the bottle *A* by a stream of

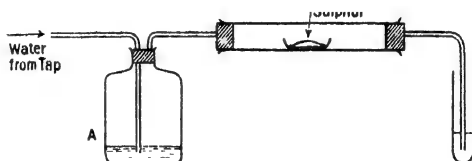


Fig. 105. Preparation of Sulphur Dioxide from Sulphur.

water from the tap; the air passes over the heated sulphur (or iron pyrites) in the boat. 0.5 gm. of sulphur or 1 gm. of iron pyrites will produce ample sulphur dioxide for the following tests.

Bubble the gas through the following contained in test-tubes:

- (1) Litmus solution.
- (2) A dilute solution of potassium permanganate.
- (3) A dilute solution of potassium dichromate.
- (4) A solution of sulphuretted hydrogen.
- (5) Water in which are placed petals of a coloured flower such as a sweet pea.

Tests (1), (2) and (3) can be performed by holding litmus paper, or strips of filter paper dipped in the solution mentioned at the mouth of the tube from which the gas is issuing. These, with the smell, are characteristic tests for the gas.

EXPERIMENT 75. Preparation from copper and sulphuric acid.

The gas can be prepared in a higher state of purity by heating copper with concentrated sulphuric acid or by adding concentrated hydrochloric acid to a sulphite—such as sodium sulphite. The apparatus for use with copper and sulphuric acid is shown in fig. 106. 3 gm. of copper and 9 c.c. of concentrated sulphuric acid will produce 1000 c.c. of gas. Collect the gas by displacement of air (it is soluble in water and heavier than air), passing it to the bottom of a jar standing with its mouth upwards.

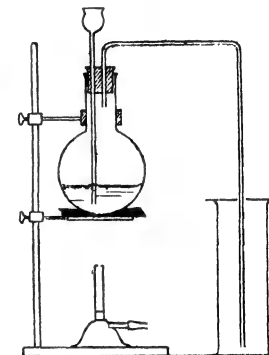


Fig. 106. Preparation of Sulphur Dioxide.

Collect two or three small jars and examine it as follows:

(6) Insert a burning taper into a small jar.

(7) Invert over a small jar of the gas another filled with sulphuretted hydrogen, and withdraw the plates.

Also carry out tests (1), (2) and (3) above, either by bubbling the gases through the liquids or by means of filter paper which has been dipped in the solutions.

Also

(8) Bubble the gas through a test-tube about nine-tenths full of water. Observe how the bubbles decrease in size as they rise.

(9) Repeat (8) with caustic soda solution.

672. Other methods of preparation. The preparation of sulphur dioxide from a sulphite and concentrated hydrochloric acid can conveniently be performed on a test-tube scale (see fig. 107). Tests (1), (2) and (3) (§ 671) should be performed.

Similar results can be obtained with sodium thiosulphate ("hypo") and concentrated hydrochloric acid, but in this case sulphur is liberated in addition to sulphur dioxide.

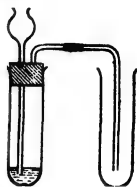


Fig. 107.

673. Volumetric composition of sulphur dioxide. A method of proving that the volume of sulphur dioxide produced when sulphur burns in oxygen is equal to the volume of oxygen used is similar in every detail to that described in § 658 for carbon dioxide, except that a piece of sulphur is used instead of a piece of charcoal. This may be made a basis for the justification of the formula SO_2 . Refer to fig. 96.

There is one very interesting observation which may be made. If the pyrex tube *A* is small, the levels of the mercury in the two limbs of the manometer will be almost exactly the same at the end of the experiment. But if the pyrex tube *A* is a large one and therefore contains much oxygen, it will be found that a small contraction occurs. This is due to the formation of a small quantity of sulphur trioxide mixed with the sulphur dioxide. This can be proved by shaking the gas in the tube *A* at the end of the experiment with a few c.c. of water and testing the solution with a few drops of barium chloride solution, acidified with hydrochloric acid. A white precipitate in these circumstances indicates the presence of sulphur trioxide.

SULPHURIC ACID

674. Properties. It is not necessary to prepare sulphuric acid in the laboratory in order to examine its properties. It is a very corrosive substance and care must be taken in using it.

EXPERIMENT 76. Examine some concentrated sulphuric acid as follows:

(1) Observe its colour, and that it is oily and heavy.

(2) Put about 20 c.c. of distilled water in a beaker and take the temperature. Add *carefully* a few c.c. of the concentrated acid; stir with a glass rod and again take the temperature. What you observe should convince you of the importance of taking great care when mixing sulphuric acid with water. *If you have to mix the acid with water, always add the acid to the water and never add the water to the acid; add the acid slowly and with stirring.*

(3) Put a small piece of sugar in an evaporating basin, add a few c.c. of concentrated sulphuric acid and warm gently. Observe carefully what happens.

You have already (Exp. 35) carried out a number of tests with dilute sulphuric acid which are common to all acids.

Perform the following test with dilute sulphuric acid:

(4) Add to a small quantity of barium chloride solution a few drops of dilute sulphuric acid. Note the precipitate which is formed. See whether the precipitate is dissolved (a) on heating, (b) by adding more of the dilute sulphuric acid.

Repeat with a solution of barium chloride to which a little dilute nitric acid has been added before the dilute sulphuric acid is added.

Repeat again, but this time add a few c.c. of dilute hydrochloric acid before adding the dilute sulphuric acid.

SULPHATES

675. The above test (4) can be used to identify a soluble sulphate. Proceed as follows:

EXPERIMENT 77. Make a solution of the sulphate in water; add about 1 c.c. of dilute hydrochloric acid and 2 or 3 c.c. of barium chloride solution.

If you wonder why the addition of dilute hydrochloric acid is necessary, add to a solution of sodium carbonate 2 or 3 c.c. of barium chloride solution. Observe the precipitate that is formed and then add dilute hydrochloric acid until the solution becomes clear again.

Repeat also with a dilute solution of sodium sulphite.

You will thus see that other salts besides sulphates will give white precipitates with barium chloride solution if the solution is neutral but not if it is acid.

SULPHITES

676. All sulphites evolve sulphur dioxide when they are warmed with dilute sulphuric acid or dilute hydrochloric acid. The tests for this gas have already been given (Exp. 74).

SULPHURETTED HYDROGEN

677. Preparation.

The gas is poisonous and must be prepared in the fume cupboard.

EXPERIMENT 78. The most convenient method of preparation consists in pouring concentrated hydrochloric acid on fragments of iron sulphide which have been covered with water. Heat is not required. The preparation can be carried out on a test-tube scale; jars of the gas need not be collected. If, however, jars are required, use the apparatus of fig. 108 and collect the gas by displacement of air (it is soluble in water and heavier than air), passing it to the bottom of a jar standing with its mouth upwards.

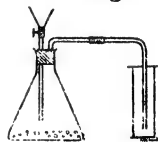


Fig. 108. Preparation of Sulphuretted Hydrogen.

Properties. The gas is obviously colourless and has a characteristic smell. Remember that it is poisonous and do not inhale it.

Examine the gas as follows:

(1) Burn it at a jet (see fig. 109). Hold in the flame a piece of an old porcelain basin; observe the deposit;

Or burn it in a jar and observe the deposit.

(2) Hold in the gas a piece of damp litmus paper and then a piece of paper which has been dipped in lead acetate solution.

(3) Pass it into chlorine water;

Or invert a jar of chlorine over a jar of the gas and remove the plates.

In either case, observe the deposit.

(4) Pass it through a test-tube nine-tenths full of water. Observe how the bubbles decrease in size as they rise.

(5) Repeat (4) with caustic soda solution.

(6) Pass it in turn through solutions of lead acetate, copper sulphate, cadmium chloride, mercuric chloride.

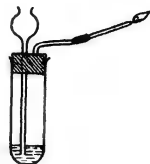


Fig. 109. Burning Sulphuretted Hydrogen.

Chapter LII

IDENTIFICATION OF GASES

678. It is often necessary to identify the gases which are evolved in a chemical reaction. This is not a difficult matter if a definite scheme is adopted such as the one outlined below. The gases chlorine, nitrogen peroxide, carbon dioxide, sulphuretted hydrogen, hydrogen chloride, ammonia, sulphur dioxide have such strongly marked characteristics that it is possible to identify them without collection in jars. On the other hand, collection of at least two small jars is desirable in the cases of hydrogen, carbon monoxide, oxygen, nitrogen, and nitrous oxide; this is particularly necessary if steam is evolved with the gas. The apparatus shown in figs. 58 or 103 should be used.

It is unwise to rely on one test; confirmation tests should always be tried.

The solubility of a gas in water can be tested by bubbling it through water in a test-tube; begin with the delivery tube just under the water, pushing it further down if the gas does not appear very soluble.

679. Gases can be divided into five groups, according to their colour, smell and inflammability:

GROUP I. Coloured. Chlorine and nitrogen peroxide.

GROUP II. Colourless without smell, burning in air.

Hydrogen and carbon monoxide.

GROUP III. Colourless, without smell, not burning in air.

Oxygen, nitrogen, nitrous oxide, nitric oxide, carbon dioxide. (Nitrous oxide has a faint smell.)

GROUP IV. Colourless, with smell, burning in air.

Sulphuretted hydrogen.

GROUP V. Colourless, with smell, not burning in air.
Hydrogen chloride, ammonia and sulphur dioxide.

680. The following are the chief tests which can be employed:

GROUP I.

Chlorine: yellowish green colour, smell, bleaches damp litmus, liberates iodine from potassium iodide and so turns starch iodide paper blue or black.

Nitrogen peroxide: reddish brown, acid to litmus, easily soluble in water; also liberates iodine from potassium iodide.

GROUP II.

Hydrogen burns with an almost colourless flame; very light and quickly escapes from a gas jar on removing the plate.

Carbon monoxide burns with a blue flame, producing carbon dioxide which will turn lime water milky. Absorbed by an ammoniacal solution of cuprous chloride.

GROUP III.

Oxygen rekindles a glowing splinter, insoluble in water, forms brown fumes with nitric oxide, absorbed by alkaline pyrogallol.

Nitrogen does not support combustion; insoluble in water, does not turn lime water milky.

Nitrous oxide rekindles a glowing splinter, somewhat soluble in water, not absorbed by pyrogallol, no fumes with nitric oxide.

Carbon dioxide does not support combustion; soluble in water, turns lime water milky.

GROUP IV.

Sulphuretted hydrogen, smell, flame produces deposit of sulphur on a piece of cold porcelain, turns lead acetate paper black.

GROUP V.

Hydrogen chloride, acid to litmus, fumes in moist air, dense white fumes with rod dipped in ammonia solution, very soluble in water, solution gives white precipitate with silver nitrate solution.

Ammonia, smell, alkaline to litmus, dense white fumes with rod dipped in hydrochloric acid, very soluble in water, solution gives blue ppt. with copper sulphate solution and brown colour or ppt. with Nessler's solution.

Sulphur dioxide, smell, acid to litmus, decolorises paper dipped in potassium permanganate, turns paper dipped in potassium dichromate green.

Chapter LIII

OXIDISING AND REDUCING AGENTS

681. Oxidising agents. The distinguishing tests for oxidising agents are based upon the capacity of these substances to (a) oxidise hydrochloric acid to chlorine, (b) oxidise hydriodic acid to iodine, (c) oxidise a ferrous salt to a ferric salt, (d) oxidise chromium hydroxide to chromic acid H_2CrO_4 .

It is not advisable to rely on one test.

EXPERIMENT 79. The tests are carried out in test-tubes as follows:

(1) Heat with concentrated hydrochloric acid and test for chlorine (§ 680).

(2) Add a solution of the substance to a solution of potassium iodide acidified with dilute sulphuric acid. Test for iodine with starch paper.

(3) Make a solution of ferrous sulphate and add a *small* piece of ferric alum; then add a drop of potassium thiocyanate solution; a faint red colour should result. Add a solution of the substance to be tested and half of 1 c.c. of dilute H_2SO_4 ; warm the liquid. The red colour will be increased by an oxidising agent.

(4) Make a dilute solution of chrome alum, add about 0.5 c.c. of NaOH solution, and some of the substance to be tested. Heat; then make the solution slightly acid with dilute H_2SO_4 . The solution will now be yellow in colour if the substance tested is an oxidising agent. The yellow colour is due to the formation of sodium chromate Na_2CrO_4 . This test can be extended by adding about 0.5 c.c. of ether and 0.5 c.c. of dilute hydrogen peroxide solution. A blue colour indicates that the substance tested is an oxidising agent.

682. Reducing agents. The distinguishing tests for reducing agents are based upon the capacity of these substances to (a) reduce potassium permanganate (in acid solution) to manganese sulphate, (b) reduce chromic acid to chromium sulphate, (c) reduce a ferric salt to a ferrous salt.

EXPERIMENT 80. The tests are carried out as follows in test-tubes:

(1) Warm the substance with a dilute solution of potassium permanganate acidified with dilute H_2SO_4 . The colour of the solution will be destroyed by a reducing agent.

(2) Warm the substance with a dilute solution of potassium chromate (or di-chromate) acidified with dilute H_2SO_4 . The colour will be changed from yellow to green by a reducing agent.

(3) Make a solution of ferrous sulphate and add a very small piece of ferric alum; then add a drop of potassium thiocyanate solution; a red colour should result. Add a solution of the substance to be tested and 0.5 c.c. of dilute H_2SO_4 ; warm the liquid. The red colour will be destroyed by a reducing agent (this test is the opposite of test (3) for an oxidising agent).

(4) [This test is a variation of test (3) above.] Wash one or two crystals of potassium ferricyanide twice with distilled water and then dissolve the remainder in distilled water. Add half of 1 c.c. of ferric chloride solution; the liquid should now be a dark brownish green. [If it is blue, the potassium ferricyanide crystals have not been sufficiently washed and a new solution must be made.] Add the substance to be tested and warm the liquid. A blue precipitate or colour will be produced by a reducing agent, ferric chloride having been reduced to ferrous chloride, which forms a blue precipitate with potassium ferricyanide.

Organic reducing agents will form (a) a red precipitate of cuprous oxide when warmed with Fehling's solution, (b) a silver mirror when warmed with a solution of silver nitrate in ammonia.

683. The tests can be tabulated in the following manner:

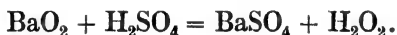
Test	Oxidising agent	Reducing agent
Solution of HCl	Cl_2 liberated	No effect
Solution of HI	I_2 liberated	No effect
Solution of FeSO_4 , trace of $\text{Fe}_2(\text{SO}_4)_3$, and KCNS	Red colour deepened	Red colour destroyed
Solution of FeCl_3 and potassium ferricyanide	No effect	Blue colour
Solution of potassium permanganate and dilute H_2SO_4	No effect	Colour destroyed
Solution of potassium chromate and dilute H_2SO_4	No effect	Colour changed from yellow to green

Chapter LIV

HYDROGEN PEROXIDE

684. Preparation. A solution of hydrogen peroxide can be prepared by the action of dilute sulphuric acid on barium peroxide.

EXPERIMENT 81. Weigh out 4 gm. of barium peroxide and make it into a thin paste by stirring in a mortar with ice cold water. The paste is added with stirring to about 100 c.c. of distilled water into which has been carefully measured 1.3 c.c. of concentrated sulphuric acid:



The precipitate of barium sulphate is allowed to settle and the clear liquid is poured through two filter papers folded together (or through a special filter paper prepared for filtering barium sulphate).

Properties. As solutions of hydrogen peroxide can be purchased, it is not necessary to prepare your own solution in order to examine its properties.

EXPERIMENT 82. The following tests should be performed either with the laboratory dilute solution or your own. A solution of hydrogen peroxide usually contains acid which prevents decomposition.

(1) Add to 5 c.c. of hydrogen peroxide solution a dilute solution of ammonia drop by drop until the liquid is just alkaline to litmus. Observe the slight formation of bubbles of gas. Add a little manganese dioxide and identify the gas which is evolved. (Collect some of it in a small jar, if you cannot identify it otherwise.)

(2) Repeat the test with a little animal charcoal (having previously added ammonia solution as before). Again identify the gas.

The above are catalytic decompositions of hydrogen peroxide, as the manganese dioxide and charcoal can be recovered unchanged by filtering the liquid.

(3) Dip a piece of filter paper in lead acetate solution and then blacken it by exposure for a few seconds to sulphuretted hydrogen. Put the filter paper in a solution of hydrogen peroxide. The black colour will be changed to white (see § 478).

Carry out the following which are distinctive tests for hydrogen peroxide.

(4) Acidify a solution of potassium chromate with dilute H_2SO_4 and add 2 c.c. of ether. Add a few drops of hydrogen peroxide solution. Notice the blue colour which soon vanishes from the aqueous (lower) layer but persists for a longer time in the ethereal (upper) layer. The blue colour is due to the formation of per-chromic acid.

(5) Acidify a solution of potassium iodide with H_2SO_4 and add a little ferrous sulphate solution. Add a few drops of hydrogen peroxide solution. The liberation of iodine can be proved by adding starch solution or using starch paper.

Chapter LV

VOLUMETRIC ANALYSIS

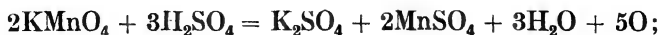
ESTIMATIONS WITH POTASSIUM PERMANGANATE

685. Potassium permanganate is a powerful oxidising agent. Its maximum oxidising power is obtained in acid solution. The only acid which can be used is sulphuric acid; nitric acid being itself an oxidising agent is inadmissible and hydrochloric acid reacts with potassium permanganate (thus using some of it) in the presence of ferrous salts and produces chlorine.

Potassium permanganate is a particularly convenient reagent for volumetric work, as on account of its strong colour the addition of a very slight excess of it can be detected by the pink tinge given to the solution. No other indicator is necessary.

It is important to remember at the outset that sufficient sulphuric acid must be present in all solutions which are to be titrated with potassium permanganate. If a brown colour is produced when potassium permanganate is added, it is a clear indication that insufficient acid has been used.

In the definition which we gave before of a normal solution we stated that a gramme-equivalent weight of the dissolved substance was contained in a litre. The question now to be considered is "what is the equivalent weight of potassium permanganate?" It is the weight of that compound which will yield an equivalent weight of oxygen in the presence of an oxidisable substance. In order to find this weight it is convenient to recall that *in the presence of an oxidisable substance* potassium permanganate reacts in the following way:



it is necessary to point out that the oxygen is not liberated

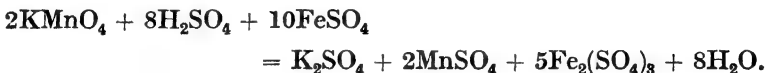
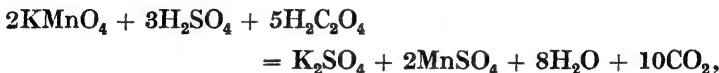
in the gaseous condition but reacts with the oxidisable substance in solution (see § 491). Thus with oxalic acid, the oxygen reacts:



Similarly with ferrous sulphate:



The complete equations are:



To return to the question of the equivalent weight of potassium permanganate, it appears from the equation



that 316 gm. of potassium permanganate yield 80 gm. of oxygen or 31.6 gm. of potassium permanganate yield 8 gm. of oxygen. A litre of normal solution will contain 31.6 gm. of the solid; it is usual, however, to employ a deci-normal solution containing 3.16 gm. per litre.

EXPERIMENT 83. Preparation of a solution of potassium permanganate.

Potassium permanganate can be obtained in a very fair degree of purity and an approximately deci-normal solution can be prepared by weighing 3.16 gm. of finely powdered solid, dissolving it in water in a beaker and making the solution up to 1 litre.

Although the potassium permanganate is fairly pure, it cannot be relied upon and the solution must be standardised in one of the following ways.

When titrating with potassium permanganate it is usual to

put that solution in the burette; the burette must, however, have a glass tap; rubber tubing is inadmissible, as the rubber reacts with the permanganate.

The permanganate solution keeps well if it is stored in bottles of blue glass.

EXPERIMENT 84. Standardisation of a solution of potassium permanganate by means of oxalic acid.

Make 250 c.c. of $N/10$ oxalic acid as described in Exp. 48.

Measure 20 c.c. of it into a conical flask (use a safety pipette or a burette, as oxalic acid is very poisonous). Add 1 c.c. of concentrated sulphuric acid and heat the solution to about 60° or 70° C. Run in the potassium permanganate solution from the burette until a permanent pink tinge is produced in the solution. The first titration should be a rough one, followed by three careful ones, as described in § 642.

The concentration of the potassium permanganate solution can be calculated from the amount of the solution used.

If 20 c.c. of $N/10$ oxalic acid require 21.2 c.c. of the potassium permanganate solution, the latter is

$$\frac{20}{21.2} N/10 \text{ or } 0.943 N/10$$

and contains 2.98 gm. of potassium permanganate solution per litre. The concentration should be clearly marked on the label.

Remember that when a solution of oxalic acid or a solution of an oxalate is titrated with potassium permanganate the solution must always be heated to 60° or 70° C.

EXPERIMENT 85. Standardisation of a solution of potassium permanganate by means of ferrous ammonium sulphate.

Ferrous sulphate is readily oxidised not only by oxidising agents but by the oxygen of the air. It is therefore not easy to obtain in a sufficiently pure condition for use as a standardising

substance. A more suitable salt, which can be obtained in a high degree of purity, is the double salt, ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

The molecular weight of this salt is 392 and contains 56 parts of iron or one-seventh of its weight of iron—a very convenient coincidence. Referring back to the equation it will be seen that 10 gramme-molecules of it are oxidised by 80 gm. of oxygen or 1 gramme-molecule by 8 gm. of oxygen. A decinormal solution will therefore contain 39.2 gm. per litre. For 250 c.c. we shall require 9.8 gm. of the salt. It is necessary to use distilled water which has been boiled to free it from dissolved air.

Weigh accurately 9.8 gm. of ferrous ammonium sulphate; dissolve it in air-free water, add 10 c.c. of concentrated sulphuric acid, and make up to 250 c.c. in a graduated flask. Titrate portions of 20 c.c. with the potassium permanganate solution (it is not necessary to heat the ferrous sulphate solution before titration) and calculate the concentration of the potassium permanganate solution as follows.

Suppose that 20 c.c. of $\frac{N}{10}$ ferrous ammonium sulphate solution react with 21.2 c.c. of potassium permanganate solution.

20 c.c. of $\frac{N}{10}$ ferrous ammonium sulphate solution contain $\frac{39.2 \times 20}{1000} \times \frac{1}{7}$ or 0.112 gm. of iron.

But 56 gm. of iron are equivalent to 31.6 gm. of KMnO_4 ,
 \therefore 0.112 gm. of iron is equivalent to $\frac{31.6 \times 0.112}{56}$ or 0.0632 gm. KMnO_4 .

\therefore 21.2 c.c. of KMnO_4 solution contain 0.0632 gm. KMnO_4
 and 1000 c.c. contain $\frac{0.0632 \times 1000}{21.2}$ or 2.98 gm. KMnO_4 .

686. The concentration of any solution of oxalic acid or an oxalate or of any solution of a ferrous salt (not containing a

chloride) can be determined by means of a standard solution of potassium permanganate. It is well to remember that:

2 molecules of potassium permanganate are equivalent to

	5 atoms of oxygen
or	5 molecules of oxalic acid
or	5 oxalate radicals
or	10 molecules of a ferrous salt
or	10 atoms of ferrous iron.

EXPERIMENT 86. Determination of iron in the ferric state.

Potassium permanganate can only be used directly to determine the amount of iron in the ferrous state. If the iron is present in the ferric state, it must be reduced to the ferrous state. The most suitable reducing agent is zinc and sulphuric acid.

Four portions of 20 c.c. of the solution to be estimated are placed in four conical flasks and each is diluted to about 100 c.c. Plenty of granulated zinc (free from iron) is added, the liquid brought to boiling and dilute sulphuric acid added from time to time to keep up a steady evolution of hydrogen. After 10 min. a drop of the solution is withdrawn on a glass rod and tested on a white tile with a drop of a solution of ammonium thiocyanate. When reduction is complete there will be no coloration, but so long as there is any ferric salt in solution a blood red coloration will be produced.

Filter each solution into a clean conical flask through a funnel plugged with glass wool. Wash the original flasks and the glass wool thoroughly with distilled water, allowing the washings to run into the conical flasks. Titrate each solution with potassium permanganate. The first titration can be a rough one, followed by three carefully performed. Hence calculate the weight of iron in a litre of the original solution.

EXPERIMENT 87. Estimation of the weights per litre of ferrous and ferric iron in a solution containing both ferrous and ferric salts.

(i) Estimate the ferrous iron by titration with standard potassium permanganate.

(ii) Take four portions of 20 c.c. of the solution, reduce each separately with zinc and sulphuric acid and estimate the *total* weight of iron per litre. Hence find by difference the weight of iron in the ferric state.

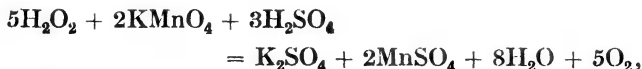
EXPERIMENT 88. Estimation of an oxalate in solution.

Proceed exactly as in the titration of oxalic acid, but be specially careful to have enough sulphuric acid present. The sulphuric acid liberates oxalic acid from the oxalate and this is then oxidised by the potassium permanganate.

Remember that two molecules of potassium permanganate are equivalent to five molecules of oxalic acid or 5 oxalate radicals C_2O_4 .

EXPERIMENT 89. Estimation of solutions of hydrogen peroxide.

Hydrogen peroxide reacts with potassium permanganate in accordance with the equation



that is to say $2KMnO_4$ are equivalent to $5H_2O_2$ or 316 gm. of permanganate are equivalent to 170 gm. of hydrogen peroxide; and one litre of $N/10$ $KMnO_4$ is equivalent to 1.7 gm. of hydrogen peroxide.

The concentrations of solutions of hydrogen peroxide are indicated by the volume of oxygen they will yield; thus a litre of 20 volume solution will yield 20 litres of oxygen. A 20 volume solution is approximately 3.5 N and can easily be diluted to approximately deci-normal concentration. But if you have no

idea of the concentration of the solution, measure out 1 c.c. with a pipette or burette and titrate it roughly. Calculate what volume of the solution will form 250 c.c. of approximately decinormal solution; measure that volume into a 250 c.c. graduated flask, fill up with distilled water and *mix* thoroughly.

Take portions of 20 c.c. of the diluted solution, add dilute sulphuric acid and titrate with a standard solution of potassium permanganate. Calculate the concentration of the diluted solution with the aid of the equation and then calculate that of the original solution.

687. Exercises in the use of a standard solution of potassium permanganate.

(1) Determine the percentage of ferrous iron in the given ferrous salt (crystalline ferrous sulphate will be suitable).

About 3 gm. of ferrous sulphate in 100 c.c. will give an approximately $N/10$ solution.

(2) Determine the percentage of oxalate radical (C_2O_4) in the given soluble oxalate (sodium oxalate).

About 0.7 gm. of sodium oxalate in 100 c.c. will give an approximately $N/10$ solution.

(3) Determine the weight of ammonium oxalate which requires 8 gm. of oxygen for complete oxidation.

About 0.7 gm. of ammonium oxalate in 100 c.c. will give an approximately $N/10$ solution.

(4) Determine the weight of potassium permanganate required to oxidise 1 gm. of potassium tetroxalate.

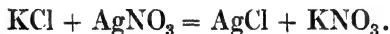
About 0.6 gm. of potassium tetroxalate in 100 c.c. will give an approximately $N/10$ solution.

Chapter LVI

VOLUMETRIC ANALYSIS (Cont.)

ESTIMATIONS WITH SILVER NITRATE

688. Solutions of silver nitrate find extensive use in volumetric analysis for the estimation of soluble chlorides, bromides or iodides. Thus a solution of potassium chloride reacts with a solution of silver nitrate in accordance with the equation



Silver chloride, and also silver bromide and iodide, are insoluble in water. They will also coagulate when shaken; it is therefore possible to ascertain when the precipitation is complete by adding the solution of silver nitrate very carefully and observing whether any further precipitation takes place. This method is the most reliable and would be adopted in any very accurate work.

A more rapid method is to add a few drops of a solution of potassium chromate to the liquid undergoing titration. Silver chromate is insoluble in water but less insoluble than silver chloride; when all the chloride has been precipitated the addition of a further drop of silver nitrate solution will cause the precipitation of dark red silver chromate. There is, however, one very serious limitation to the use of this method and that is that the solution must be exactly neutral as silver chromate is soluble in dilute acids and any alkali would cause the precipitation of silver oxide. The method cannot be employed for the estimation of hydrochloric acid in solution unless the acid is neutralised by adding a slight excess of calcium carbonate. This will convert the hydrochloric acid into soluble calcium chloride which is precipitated quantitatively by silver nitrate.

689. There is another method of estimating chlorides (or bromides or iodides) in acid solution, called Volhard's method. For a description of that method reference must be made to a book on Volumetric Analysis (A. J. Berry, *Volumetric Analysis*, C. U. Press).

EXPERIMENT 90. Preparation of a deci-normal solution of silver nitrate.

Silver nitrate can be obtained in a high degree of purity by recrystallisation; a standard solution of it can therefore be prepared by direct weighing. The molecular and equivalent weights of the salt are the same, viz. 170; a deci-normal solution contains 17 gm. per litre.

Weigh accurately 8.5 gm. of the salt; dissolve it in distilled water and make up to 500 c.c. in a graduated flask.

EXPERIMENT 91. Estimation of the percentage of chlorine in pure sodium chloride.

Take a few grammes of pure sodium chloride and dry it by heating gently in a clean evaporating basin. Weigh accurately about 3 gm. of it, dissolve in distilled water and make up to 500 c.c. in a graduated flask. Titrate portions of 20 c.c. with $N/10$ silver nitrate solution. It is best to carry out the titration in a porcelain basin, stirring with a glass rod. Add one drop of potassium chromate solution as an indicator.

After the titrations have been finished take 20 c.c. of distilled water, add one drop of potassium chromate solution and run in silver nitrate solution very carefully until the same colour is obtained as before. Subtract the volume of silver nitrate thus used from the mean volume used in the titrations.

170 gm. of silver nitrate react with 35.5 gm. of chlorine (as chloride, or more exactly as chloride ions).

EXPERIMENT 92. Estimation of a solution of hydrochloric acid and nitric acid (approximately deci-normal).

Proceed as follows:

(1) Find the volume of a standard solution of caustic soda required to neutralise the acids in 20 c.c.

(2) Neutralise the acids by adding a slight excess of calcium carbonate; titrate the chloride in the resulting liquid with $N/10$ AgNO_3 , using potassium chromate as indicator.

From the second result calculate the weight of hydrochloric acid in 20 c.c. of the solution; from this calculate the volume of standard caustic soda solution which would have neutralised the hydrochloric acid alone. Subtraction will give the volume of standard caustic soda which would have neutralised the nitric acid alone; from this calculate the weight of nitric acid in 20 c.c. of the solution. State finally the weights of the two acids in 1 litre.

690. Exercises in the use of a standard solution of silver nitrate.

(1) Determine the equivalent weight of ammonium chloride by titration with a standard solution of silver nitrate (about 0.5 gm. of ammonium chloride in 100 c.c. will give an approximately $N/10$ solution).

(2) Determine the percentage of chlorine in potassium chloride by titration with a standard solution of silver nitrate (about 0.8 gm. of potassium chloride in 100 c.c. will give an approximately $N/10$ solution).

Chapter LVII

IDENTIFICATION OF SALTS

IDENTIFICATION OF ACID OR NEGATIVE RADICALS

691. In analysing an unknown salt of a metal it is necessary to identify both the positive (or metallic) and the negative (or acid) radicals; these identifications must usually be performed separately. The tests for acid radicals depend to some considerable extent upon the identification of gases particulars of which were given in §§ 678–680.

It is necessary to emphasise that success in this branch of chemistry can only be achieved by following a definite system. Haphazard testing is a waste of time and can rarely give results in which the worker can feel any confidence. It is also necessary to emphasise the importance of not relying on one test; every suspicion should be fully confirmed. Further, it is inadvisable to rely on one's sense of smell, which can easily be deceived. It follows therefore that if a gas is evolved, all the tests and not merely one must be used to identify it. Waste of time and disappointment will also be avoided if clean test-tubes are always used.

692. Tests to be applied.

(1) Treat the solid substance with dilute sulphuric acid in the cold. Afterwards heat.

Gas evolved	Acid radical	Confirmatory tests with original substance
CO ₂ in the cold	Carbonate or bicarbonate	Bicarbonates give off CO ₂ when boiled with water
Cl ₂ in the cold	Hypochlorite	Add some of the substance to a solution of MnSO ₄ and warm (see § 655)

Gas evolved	Acid radical	Confirmatory tests with original substance
H_2S	Sulphide	If soluble in water, will give violet colour with sodium nitro-prusside
SO_2 alone	Sulphite	No further confirmation (solutions of sulphites, unless freshly made, contain sulphates and may give reactions of sulphates)
SO_2 plus deposit of sulphur	Thiosulphate	Decolourises a solution of iodine in potassium iodide
NO_2	Nitrite	Mix a solution of the substance with a solution of ferrous sulphate, acidified with dilute H_2SO_4 . Brown colour in cold

(2) If no gas is evolved with dilute sulphuric acid, heat the solid substance with concentrated sulphuric acid (do not heat so strongly that the sulphuric acid is decomposed). The concentrated sulphuric acid must be added with care; if a chlorate is present, a yellow gas ClO_2 will be evolved as soon as H_2SO_4 is added; this gas is explosive. If this yellow gas is produced, do not heat the substance but empty the test-tube at once into the sink.

Gas evolved	Acid radical	Confirmatory tests with original substance
ClO_2 (yellow)	Chlorate	(1) Heat substance <i>alone</i> ; it will evolve oxygen, leaving a chloride (see § 656) (2) Add concentrated HCl (see § 656)
NO_2 (reddish brown)	Nitrate	(1) Mix solid with copper turnings and concentrated H_2SO_4 ; NO_2 more freely evolved (2) Brown ring test (§ 663).

Gas evolved	Acid radical	Confirmatory tests with original substance
Acetic acid vapour (smell of vinegar)	Acetate	(1) Make a neutral solution; add FeCl_3 solution—red colour (2) Mix substance with 1 c.c. of alcohol and 2 c.c. of concentrated H_2SO_4 and warm—pleasant smell of ethyl acetate
HCl	Chloride	(1) Add to solution 1 c.c. of dilute HNO_3 and 1 c.c. of silver nitrate solution—white precipitate (2) Mix solid with manganese dioxide and add concentrated H_2SO_4 —chlorine evolved
Bromine vapour, mixed with SO_2 and HBr	Bromide	Add to solution 1 c.c. of dilute HNO_3 and 1 c.c. of silver nitrate solution—yellowish precipitate
Iodine vapour, mixed with SO_2 and HI	Iodide	Add to solution 1 c.c. of dilute HNO_3 and 1 c.c. of silver nitrate solution—yellow precipitate
CO_2 and CO	Oxalate	Make a neutral solution of the salt and add calcium chloride solution—white precipitate

(3) If no gas is evolved either with dilute or concentrated sulphuric acid, the acid radical is probably a sulphate, a phosphate, a chromate, a di-chromate or a permanganate.

Test for these as follows:

Sulphate: add to the solution 2 c.c. of dilute HCl and 2 c.c. of barium chloride solution—white precipitate.

Phosphate: warm the solution with 1 c.c. of concentrated nitric acid and 2 c.c. of ammonium molybdate solution—yellow precipitate. (See also § 400.)

Chromate or Dichromate: (1) Add to the neutral solution a solution of barium chloride—yellow precipitate. (2) Repeat with lead acetate solution—yellow precipitate. (3) Add to the dilute solution about 1 c.c. of dilute H_2SO_4 , about 0.5 c.c. of ether and a few drops of H_2O_2 —blue colour.

Permanganate: Purple colour in solution is removed by (a) SO_2 , (b) hydrogen peroxide and dilute H_2SO_4 , (c) ferrous sulphate and dilute H_2SO_4 , (d) oxalic acid and dilute H_2SO_4 .

Chapter LVIII

IDENTIFICATION OF SALTS (Cont.)

IDENTIFICATION OF METALLIC IONS OR POSITIVE RADICALS

693. Here again success can only be attained by working on a definite system and by exercising intelligence. Haphazard "spotting" is a waste of time. The intelligent use of the preliminary examination will often give full information about the identity of the compound under examination.

Before proceeding to describe the preliminary examination of a solid it is necessary to give a few instructions as to how these tests should be carried out.

694. Heating on charcoal.

A small hole is scooped out of the charcoal block. In it is placed a little of the substance to be tested. The holes of the Bunsen burner are closed and a mouth blowpipe is used to direct the flame on to the charcoal block at a point where the substance touches the charcoal and not on to the top of the substance. In this way the full reducing action of red hot charcoal is obtained.

In the third test (see § 700) the substance is mixed with anhydrous sodium carbonate and is heated as described above.

695. Flame tests. The flame tests are performed by putting a small portion of the substance on a clean platinum wire and heating it in the Bunsen flame*. The best way to clean the wire is to put a few drops of concentrated hydrochloric acid in a watch-glass, dip the wire in the acid, and heat it in a Bunsen flame, dip it in the acid again and heat once more. This process is repeated until there is no colour produced by putting the wire in

* Rods of infusible porcelain are now available which are very satisfactory substitutes for platinum wires.

the flame. Having cleaned the wire, do not finger it or put it on the bench. Wash the watch-glass with distilled water, and put into it a little of the substance to be examined, moisten it with dilute hydrochloric acid, dip the wire into the mixture and then heat it in a Bunsen flame. Observe the colour of the flame directly and through cobalt glass.

696. Borax bead tests. The bead is formed on a clean platinum wire by bending the end into a small loop, heating it in a flame and dipping it while hot into powdered borax. The wire with the borax is again heated in the flame when a clear bead will be formed. A very small portion of the unknown substance is placed on the bead, which is then heated by means of a mouth blowpipe. It is important not to use much of the substance under examination, otherwise the bead may be so dark that its colour cannot be ascertained.

697. System of identification of positive (metallic) radicals. After the preliminary tests have been carried out the substance is examined in solution. The system depends on the insolubility of the chlorides, sulphides, hydroxides and carbonates. It will be better understood after the following experiments have been performed.

698. Precipitation of insoluble compounds.

EXPERIMENT 93. Carry out these tests in test-tubes and note after each whether a precipitate is produced.

(1) (a) To a solution of silver nitrate add $\frac{1}{2}$ c.c. of dilute HCl.

(b) Repeat with a solution of lead nitrate or lead acetate.

(2) (a) To a solution of copper sulphate add $\frac{1}{2}$ c.c. of dilute HCl. Now pass H_2S through the solution.

(b) Repeat with a solution of cadmium sulphate.

(3) (a) To a solution of ferric chloride add dilute HCl and then pass H_2S .

(b) To a fresh portion of ferric chloride solution add 2 c.c. of a strong solution of ammonium chloride and $\frac{1}{2}$ c.c. of ammonium hydroxide.

(c) Repeat with aluminium sulphate.

(4) (a) To a solution of zinc sulphate add dilute HCl and pass H_2S .

(b) To a fresh portion of zinc sulphate solution add 2 c.c. of a strong solution of ammonium chloride and $\frac{1}{2}$ c.c. of ammonium hydroxide.

(c) Now add to the solution in (b) a solution of ammonium sulphide.

(d) Repeat with nickel sulphate.

(5) (a) Test a solution of calcium chloride as in (4) (a), (b) and (c).

(b) To a third portion of calcium chloride solution add ammonium chloride solution, ammonium hydroxide and a small piece of ammonium carbonate and heat.

(c) Repeat with barium chloride.

699. Groups and reagents. You are now in a position to understand the division into groups and the reagents which are chosen for each group.

Group	Reagent	Precipitates obtained of
I	Dilute HCl	Metals whose chlorides are insoluble in dilute HCl, viz. lead, silver, mercury (-ous)
II	Dilute HCl and H_2S	Metals whose chlorides are soluble in dilute HCl, but whose sulphides are insoluble in dilute HCl, viz. mercury (-ic), copper, bismuth, cadmium, tin, arsenic, antimony
III	NH_4Cl and NH_4OH	Metals whose chlorides and sulphides are soluble in dilute HCl, but whose hydroxides are insoluble in NH_4Cl and NH_4OH , viz. iron, aluminium, chromium

Group	Reagent	Precipitates obtained of
IV	NH_4Cl , NH_4OH and $(\text{NH}_4)_2\text{S}$	Metals whose chlorides and sulphides are soluble in dilute HCl , whose hydroxides are soluble in NH_4Cl and NH_4OH , but whose sulphides are insoluble in an alkaline liquid, viz. zinc, manganese, nickel, cobalt
V	NH_4Cl , NH_4OH and $(\text{NH}_4)_2\text{CO}_3$	Metals whose chlorides are soluble in dilute HCl , whose sulphides are soluble both in acid and alkaline liquids, whose hydroxides are soluble in NH_4Cl and NH_4OH , but whose carbonates are insoluble in an alkaline liquid, viz. calcium, strontium, barium

The question may be asked “how can the different metals which give precipitates in the same group be distinguished?” the answer is “partly by the colour of the precipitate and partly by confirmatory tests”.

700. Identification of the positive radical of an unknown salt. You are now in a position to examine an unknown substance.

Preliminary examination of the solid.

(1) Heat on charcoal before the blowpipe:

Residue yellow when hot, white when cold Zinc

(2) Moisten residue from (1) if it is white with cobalt nitrate solution and heat again:

Residue blue	Aluminium
„ green	Zinc
„ bluish green	Tin
„ pink	Magnesium

(3) Make another hole in charcoal; mix substance with anhydrous sodium carbonate and heat before blowpipe:

Red malleable metallic spangles	Copper
Malleable metallic beads, yellow incrustation			Lead

Malleable metallic beads, without incrustation	Silver
---	--------

Malleable metallic beads, incrustation yellow when hot	Tin
Brittle metallic beads	Bismuth
Odour of garlic	Arsenic
Odour of ammonia	NH ₄

(4) Heat on platinum wire:

Flame crimson	Strontium
„ orange	Calcium
„ apple green	Barium
„ blue-green	Copper
„ intense yellow	Sodium
„ lilac	Potassium

(5) Heat on a borax bead:

Reducing flame	Oxidising flame	
Green	Green	Chromium
Blue	Blue	Cobalt
Red	Green	Copper
Colourless	Violet	Manganese
Bottle green	Reddish violet	Iron

(6) Heat a little of substance with anhydrous sodium carbonate in a dry tube:

Black mirror	Arsenic
Grey sublimate	Mercury
Odour of ammonia	NH ₄

701. Tests with a solution of the substance. The unknown substance must first be got into solution. To do this shake up a little of it with distilled water in a test-tube; if it does not dissolve in cold water, heat the water. If it does not dissolve in hot water, try to dissolve it in dilute hydrochloric acid, first cold and then hot. If that fails, try to dissolve a separate portion in

concentrated hydrochloric acid. If hydrochloric acid will not dissolve it, try dilute nitric acid; and if that fails, try concentrated nitric acid. If neither hydrochloric nor nitric acid will dissolve it, try a mixture of concentrated hydrochloric acid and nitric acid in equal proportions (*aqua regia*).

There are several points to be noticed:

(1) A gas may be evolved when the substance is treated with an acid; the liquid must be boiled to expel all the gas.

(2) The solution which is to be tested in the following scheme must not be strongly acid; excess of hydrochloric acid can be removed by boiling (in a fume cupboard); excess of nitric acid can be removed by evaporation to dryness.

(3) If *aqua regia* has been used to dissolve the substance, the liquid must be evaporated to dryness and the residue dissolved in water.

702. Group tests and confirmatory tests.

GROUP I. Reagent: dilute hydrochloric acid.

Precipitate may be	Further tests with precipitate	Confirmatory tests with original substance
PbCl_2 (white)	Soluble in hot water, precipitate reappears on cooling.	(1) K_2CrO_4 —yellow precipitate (2) KI —yellow precipitate dissolves on boiling
AgCl (white)	Insoluble in hot water, soluble in NH_4OH	K_2CrO_4 —crimson precipitate
Hg_2Cl_2 (white)	Insoluble in hot water, blackened by NH_4OH	Heat solid in dry tube with anhydrous Na_2CO_3 —grey sublimate

GROUP II. Reagent: dilute HCl , followed by H_2S .

Precipitate may be	Effect of shaking precipitate with ammonium sulphide solution	Confirmatory tests with original substance
HgS (black)	Insoluble	Acidulate with dilute HCl and add metallic copper—bright deposit of mercury

Precipitate may be	Effect of shaking precipitate with ammonium sulphide solution	Confirmatory tests with original substance
CuS (brownish black)	Insoluble	NH ₄ OH—blue precipitate dissolves in excess to dark blue liquid
Bi ₂ S ₃ (brownish black)	Insoluble	(1) NH ₄ OH—white precipitate (2) SnCl ₂ and NaOH—black precipitate
CdS (canary yellow)	Insoluble	NH ₄ OH—white precipitate soluble in excess
SnS (dark brown)	Soluble	Add to solution small piece of zinc and dilute HCl—grey deposit of tin
SnS ₂ (dirty yellow)	Soluble	
As ₂ S ₃ (yellow)	Soluble	Add to solution piece of copper foil and dilute HCl; boil—grey deposit on copper
Sb ₂ S ₃ (orange-red)	Soluble	Add to solution a few drops of dilute HCl and dilute freely with distilled water—white precipitate

GROUP III. *Note:* Use a fresh portion of solution; add a drop of concentrated nitric acid; if a brown colour is produced, add more nitric acid and boil. Neutralise with NH₄OH.

Reagent: a concentrated solution of NH₄Cl and then NH₄OH.

Precipitate may be	Confirmatory tests with original solution
Fe(OH) ₃ (reddish brown)	(1) Potassium ferricyanide—blue precipitate with ferrous salt (2) Potassium ferrocyanide—blue precipitate with ferric salt (3) Potassium thiocyanate—blood red coloration with ferric salt
Al(OH) ₃ (white gelatinous)	NaOH solution—white precipitate, soluble in excess
Cr(OH) ₃ (bluish green)	Add NaOH solution, then a little solid sodium peroxide and boil. Solution becomes yellow due to formation of sodium chromate (see § 692 (3))

GROUP IV. Reagent: NH_4Cl , NH_4OH and $(\text{NH}_4)_2\text{S}$.

Note: Add the ammonium sulphide very carefully, otherwise you cannot see the colour of zinc sulphide or manganese sulphide.

Precipitate may be	Confirmatory tests with original solution
ZnS (white)	NaOH solution—white precipitate, soluble in excess
MnS (flesh coloured)	(1) NaOH solution—white precipitate becoming brown on shaking in test-tube (2) Heat the solid (1 part) with two parts of fusion mixture (Na_2CO_3 and K_2CO_3) and 1 part of KNO_3 on a piece of porcelain over blowpipe—green mass on cooling
NiS (black)	NaOH solution—green precipitate Dimethyl glyoxime—red precipitate
CoS (black)	(1) NaOH solution—blue precipitate of basic salt, which changes to pink on boiling (2) Borax bead (with solid) deep blue

GROUP V. Reagent: NH_4Cl and NH_4OH and $(\text{NH}_4)_2\text{CO}_3$.

Note: As ammonium carbonate solutions do not keep well, it is best to add a small piece of solid ammonium carbonate and to heat the liquid.

Precipitate may be	Confirmatory tests with original solution
CaCO_3 (white)	(1) CaSO_4 solution—no precipitate (2) Flame test—orange red
SrCO_3 (white)	(1) CaSO_4 solution—white precipitate on standing (2) Flame test—crimson
BaCO_3 (white)	(1) CaSO_4 solution—immediate white precipitate (2) Flame test—apple green

If no precipitate is obtained with any of the group reagents, the salt may be a compound of magnesium, ammonium, sodium or potassium. This must be decided by separate tests.

Magnesium compound:

Add to original solution solutions of ammonium chloride, ammonium hydroxide and sodium phosphate—white ppt.

Ammonium compound:

Boil original substance with NaOH solution—ammonia set free

Sodium compound:

Flame test—intense yellow colour

Potassium compound:

(1) Flame test—lilac colour

(2) Add to a strong solution of original substance an equal volume of alcohol and then a strong solution of sodium perchlorate or perchloric acid—white ppt. of potassium perchlorate.

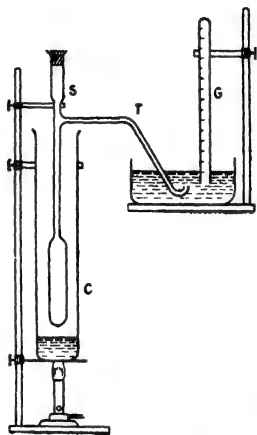
Chapter LIX

DETERMINATION OF MOLECULAR WEIGHTS

VOLATILE SUBSTANCES

703. By Victor Meyer's method.

EXPERIMENT 94. The apparatus is shown in fig. 110. The outer jacket *C* is frequently made of glass; but a metal one is more durable and just as satisfactory. The inner tube *S* is seen to consist of a cylindrical glass bulb sealed to a long tube, the upper part of which is widened to take a cork; a delivery tube is sealed into the side. Some water is placed in the outer jacket; the inner tube is dried and some dry sand or copper turnings placed at the bottom of the cylindrical bulb. The apparatus is set up and the water is boiled. A small stoppered bottle, which can pass down the long tube, is dried and weighed. About 0.5 gm. of the substance (say carbon tetrachloride) is put in the bottle, which is again weighed.



*Tube for
Liquid*

Fig. 110. Victor Meyer's Apparatus. Fig. 110 a.

[Instead of a stoppered bottle it is possible to use small bulbs made of glass tubing (see fig. 110 a). A piece of tubing which will fit easily into the long tube of the apparatus is sealed at one end and drawn out to a fine tube at the other. The bulb is weighed. It is then held in crucible tongs and warmed in a flame; some of the air will be expelled. It can then be held with the open end in the liquid under examination contained in a crucible.

As it cools, some of the liquid will be drawn into the bulb. Further warming and cooling will draw in more liquid. It should then be weighed to ascertain that the right quantity has been introduced; if this is correct, it should be sealed by holding the open end in a flame and accurately weighed.]

When no more bubbles of air issue from the delivery tube *T*, the graduated tube *G* is brought over the end of the delivery tube. The stopper of the small bottle is loosened (or the end cut off the small bulb), the cork is removed, the bottle or bulb dropped down the tube and the cork quickly replaced.

The liquid is converted into vapour, which displaces into the graduated tube an equal volume of air (a rapid evolution of air is essential to success). This air will cool in the graduated tube *G* and will then have a volume which the vapour would have occupied if it could have remained a vapour at that temperature and pressure. When no more air issues from the delivery tube, place a crucible under the end of the graduated tube and transfer it to a tall jar of water. Holding the tube in a test-tube holder, raise it until the water inside the tube and that outside are at the same level; read the volume of air. Record the temperature of the water in the jar and the height of the barometer.

The air has been collected over water and is therefore saturated with water vapour; the pressure of the air alone is the height of the barometer minus the vapour pressure of water.

Record your results as follows:

Weight of bottle + liquid	=gm.
Weight of bottle	=gm.
Weight of liquid	=(<i>M</i>) gm.
Volume of air collected	=(<i>V</i>) c.c.
Temperature	=(<i>t</i>)° C.
Barometer	=mm.
Vapour pressure of water	=mm.
Pressure of air	=(<i>p</i>) mm.
Volume of air at 0° C. and 760 mm.	=(<i>V'</i>) c.c.

M gm. of liquid when vaporised displaced V' c.c. of air measured at S.T.P. Calculate the weight of liquid which when vaporised would displace 22.4 litres of air measured at S.T.P. This is the molecular weight of the vapour.

SUBSTANCES IN SOLUTION

704. The molecular weight of a substance in solution can be determined by measuring the depression of the freezing-point of the solution (see chap. XXVIII, § 433). It has been found by experiment that the freezing-point of a solution containing 1 gramme-molecule in 1000 gm. of water is -1.85°C . If the freezing-point of a solution of known concentration (in grammes per litre) is found, it is an easy matter to calculate by simple proportion the weight of the substance which, when dissolved in 1000 gm. of water, would produce a solution having a freezing-point of -1.85°C .

The apparatus described below will give results accurate to about 2 or 3 per cent. More accurate results can be obtained with more elaborate apparatus and especially a more sensitive thermometer.

EXPERIMENT 95. Make a 10 per cent. solution of urea in water and measure 25 c.c. of it with a pipette into a boiling tube A , immersed in a freezing mixture of salt and ice (see fig. 111). Insert a thermometer T graduated in fifths of a degree. Stir the solution carefully and allow the temperature to fall about 2 degrees below 0°C . Then stir vigorously. As soon as crystals of ice begin to form in the liquid, the mercury in the thermometer will rise rapidly. The highest point reached is the freezing-point of the solution, which must be recorded. Remove the tube from the freezing mixture and allow the ice to melt; then replace it and repeat the determination.

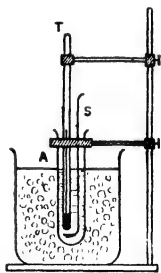


Fig. 111. Freezing-point Apparatus.

Dilute the solution with 25 c.c. of water and re-determine the freezing-point.

Let us suppose that in the first determinations, when the concentration of the solution was 10 per cent., it was found that the freezing-point was lowered by t° C.; that is, 100 gm. of urea dissolved in 1000 gm. of water lowered the freezing-point by t° C. A gramme-molecule of urea would lower it by 1.85° C. (see above); therefore the molecular weight of urea is

$$\frac{100 \times 1.85}{t}.$$

Chapter LX

L'ENVOI

The more obvious purpose of this book—to introduce the student to the principles of the Science of Chemistry—is now served. But before we take leave of him, we would invite the reader to look back and to take a brief survey of the ground covered.

On the one hand, his attention has been directed to a series of chemical facts, capable of verification by experiment, many of which it is to be hoped he has tested practically for himself. On the other hand, he has been introduced to the accepted theory which explains them. The facts must stand. Any part of the theory is open to cancellation or amendment if anyone with a wider vision can supply better explanations or lay down better principles.

The chemical facts discussed touch our familiar every-day world at countless points. A fire burning should now mean far more than a little heat, a little light, a little smoke. The student can look at the rust on an old nail or the green incrustation on a copper antique with a new light in his mind. A growing leaf, a cake of soap, a spoonful of salt all have points of contact with his newly acquired knowledge. But, at the same time, we shall be surprised if the sense of new knowledge is not accompanied by another, a sense of disappointment. There are so many things we have *not* explained, so many common objects and common substances which have *not* been investigated. A man's estimate of his progress in knowledge may be measured by a fraction, of which the numerator is what he knows and the denominator is what yet remains to be known. The more he increases the numerator, the larger does the denominator seem

to be, as he realises more and more what a vast domain there is still to explore. Thus as knowledge progresses the fraction decreases. It is this which is responsible for a real and unaffected spirit of humility in so many great men of science, so that Newton himself could say without any suspicion of pose:

"I feel like a child playing on the sea shore, now finding some prettier pebble or more beautiful shell than my companions while the unbounded ocean of truth lies undiscovered before me".

Man must keep in his mind a just balance, on the one hand a proper pride in the very considerable achievements of his race, and, on the other, a sense of the infinite vastness and variety of the problems which still lie ahead.

It is to be hoped that the reader has—quite unconsciously, no doubt—acquired a habit of believing in the laws of cause and effect and in the orderliness of Nature. That there *are* principles at the back of Nature and that there is, amid the apparent chaos and variety in the world, a real orderliness seems to us moderns quite obvious. Yet it is a secret which has been wrung from Nature only with great thought and great effort. There are still tribes on the earth who people every river, every tree with its own deity or sprite, elf or demon. Such a view of the world would make science impossible. Expressed in terms of Chemistry it could be illustrated by saying that what happened when zinc was placed in sulphuric acid depended capriciously upon the whim of a gnome imprisoned in the zinc. The great principle, to us so very simple and so very obvious—that under exactly the same set of conditions the same thing will always happen—is called the principle of the "Uniformity of Nature", and it is an unexpressed postulate behind every chemical statement in this book.

We hope the reader has been encouraged with success to cultivate in his own mind a sense and habit of order in the marshalling, the correlation and explaining of facts, and also a

sense of the essential orderliness of the world in which he has been placed. Many people can only handle facts in a foggy-minded and biased way, many people carry on the ordinary affairs of their lives as if there were no laws of cause and effect or as if they themselves would, by some dispensation of a benevolent Providence, be absolved from them. Orderliness in one's own mind and orderliness in Nature—to achieve one and to sense the other will do the reader more good than just to acquire a number of chemical facts.

One thing more. There was, more particularly during the second half of the last century, a somewhat acrid clash between science and religion. It has fortunately died down. This happy result was inevitable once it was accepted, as it should have been more readily, that the scientist was not out to prove or disprove any particular view of life but was engaged solely in a reverent and clear-eyed search for Truth. The link between science and religion lies here, that the theologian accepts from the scientist his discovery of the orderliness and the beauty behind creation and sees in it the orderliness and the beauty of the Mind of God.

“Let knowledge grow from more to more
And more of reverence in us dwell
That mind and heart according well
May make one music as before,
But vaster.”

QUESTIONS

PRINCIPALLY FROM SCHOOL CERTIFICATE PAPERS

Chapter IV

OXYGEN

1. Describe the preparation of oxygen from potassium chlorate. What is meant by the statement that manganese dioxide will act as a catalyst in this preparation?
2. How did Lavoisier show that one-fifth (by volume) of the air is oxygen?
3. How can the proportion of oxygen in air be determined?
4. By what tests can oxygen be distinguished from all other gases?
5. Give the names of (a) two oxides, and (b) two other compounds which on heating alone will give off oxygen. [London.]

Chapter V

HYDROGEN

1. Describe the preparation of hydrogen from (a) cold water, (b) boiling water, (c) steam.
2. What substances are formed when a metal (such as iron) dissolves in dilute sulphuric acid?
3. By what tests can hydrogen be distinguished from all other gases?

Chapters VI and VII

MOLECULAR THEORY

1. What is the relation between the molecular weight of a gas and its density relative to hydrogen? How can this relation be established?
2. One litre of a gas, measured at s.t.p., weighs 1.965 gm. What is the molecular weight of the gas?
3. Three litres of a gas, measured at s.t.p., weigh 4.02 gm. Calculate the molecular weight of the gas.
4. 608 c.c. of a gas, measured at 15° C. and 720 mm., weigh 0.682 gm. What is its molecular weight?
5. 290 c.c. of a gas, measured at 17° C. and 756 mm., weigh 0.775 gm. What is its molecular weight?
6. 582 c.c. of a gas, measured at 18° C. and 740 mm., weigh 0.403 gm. Calculate its molecular weight.
7. 0.77 gm. of a vapour, measured at 100° C. and 750 mm., occupy 155 c.c. What is its molecular weight?

8. 1 gm. of a vapour, measured at 120° C. and 745 mm., occupy 391.5 c.c. What is its molecular weight?

9. 1.5 gm. of a vapour, measured at 182° C. and 768 mm., occupy 330 c.c. Calculate its molecular weight.

10. 2 gm. of a vapour, measured at 197° C. and 770 mm., occupy 405 c.c. What is its molecular weight?

Chapter VIII

ATOMIC WEIGHTS

1. Determine the atomic weight of nitrogen from the following facts:

Substance	Molecular weight	Percentage of nitrogen
Nitrogen	28	100
Ammonia	17	82.4
Nitrous oxide	44	63.64
Nitric oxide	30	46.66

2. Determine the atomic weight of chlorine from the following facts:

Substance	Molecular weight	Percentage of chlorine
Chlorine	71	100
Hydrogen chloride	36.5	97.25
Mercurous chloride	236.1	15.04
Mercuric chloride	271.6	26.15
Arsenic chloride	181.5	58.7
Phosphorus chloride	137.5	77.5
Ferric chloride	325	65.5

3. Determine the atomic weight of sulphur from the following facts:

Substance	Molecular weight	Percentage of sulphur
Sulphur above 1000° C.	64	100
Sulphuretted hydrogen	34	94.1
Sulphurous anhydride	64	50
Carbon sulphide	76	84.2

4. State the Law of Multiple Proportions; how is it explained by the atomic theory?

A metal has two oxides, *A* and *B*. The following results were obtained when each of the oxides was heated to constant weight in a current of pure hydrogen:

2.00 gm. of *A* gave 0.2517 gm. of water.

1.00 gm. of *B* gave 0.2264 gm. of water.

Show that these results illustrate the above law.

[Oxford and Cambridge.]

5. The black and red oxides of mercury contain 96.15 per cent. and 92.59 per cent. of mercury respectively. Show that this statement supports the Law of Multiple Proportions. [N.U.]

6. 0.785 gm. of a chloride of mercury yielded, on reduction, 0.667 gm. of mercury.

0.678 gm. of another chloride of mercury yielded, on reduction, 0.501 gm. of mercury.

Show that the above results illustrate the Law of Multiple Proportions. [Cambridge.]

7. 0.5 gm. of one oxide of a metal when heated in a stream of hydrogen gave 0.1687 gm. of water; 0.4 gm. of the second oxide of the same metal under the same conditions gave 0.100 gm. of water.

Show that the above results illustrate the Law of Multiple Proportions. [Cambridge.]

8. An element *X* forms two chlorides containing 62.6 and 45.57 per cent. of *X* respectively. Show that these results are in accordance with the Law of Multiple Proportions.

Chapter IX

WATER

1. Describe a method of determining the composition by volume of steam. Apply Avogadro's Law to the results obtained and thus show that the molecule of oxygen contains at least two atoms. [N.U.]

2. Describe one method of finding the proportions by weight in which oxygen and hydrogen combine to form water, indicating the most important precautions which must be taken.

3. Explain the terms *hygroscopic*, *deliquescent* and *efflorescent*; give two examples of each class of compounds.

4. Sketch and describe the apparatus you would use to obtain pure water from river water. What tests would you apply to ascertain whether the sample produced was pure. [London.]

Chapter X

SOLUTION

1. If you were given a supply of crystals of a salt and a solution of that salt, how would you determine whether the solution was saturated, super-saturated or unsaturated?

2. What is meant by a saturated solution? How would you prepare a saturated solution of potassium chloride in water at room temperature and how would you ascertain what weight of salt one litre of this solution contained? [Cambridge.]

3. Describe how you would separate by crystallisation a mixture of 50 gm. of potassium chloride and 50 gm. of potassium chlorate (see fig. 21, p. 66).

4. Ordinary tap-water always contains some air in solution. Describe in detail how you would collect a quantity of this air from tap-water. How could you find the proportion by volume of oxygen in such air? Explain why the composition of this dissolved air will be different from that of ordinary air. [N.U.]

5. Explain what is meant by "water of crystallisation", giving two examples of salts containing it. State how you would determine experimentally the percentage weight of water of crystallisation in one such salt.

Chapter XI

EQUIVALENT WEIGHTS AND ATOMIC WEIGHTS

1. What is meant by the term *equivalent weight*? Describe with the aid of a sketch how you would find the equivalent weight of copper.

2. Draw a sketch of the apparatus you would use to determine the equivalent weight of a metal such as zinc, magnesium or aluminium. State what measurements must be made and what precautions taken.

3. What relation exists between the equivalent weight and the atomic weight of an element? The chloride of a metal contains 61.8 per cent. of the metal. Calculate the equivalent weight of the metal. (Equiv. wt. of chlorine = 35.5.)

The specific heat of the metal is 0.0548; calculate the atomic weight of the metal.

4. 0.25 gm. of a metal when dissolved in hydrochloric acid liberated 337 c.c. of hydrogen, collected over water and measured at 17° C. and 759.4 mm. The specific heat of the metal was found to be 0.21. Calculate (a) the equivalent weight, (b) the atomic weight of the metal.

[Cambridge.]

5. Draw an explanatory sketch of an apparatus by means of which you could determine accurately the equivalent weight of carbon.

[Cambridge.]

6. Calculate the volume of hydrogen at 10° C. and 750 mm. which could be obtained from the action of dilute hydrochloric acid on 1 gm. of a metal of which the equivalent weight is 9.

What weight of the oxide of this metal could be obtained from 2 gm. of the metal? [London.]

7. 91.46 gm. of a metal were converted into 121.50 gm. of the chloride of the metal. Calculate the equivalent weight of the metal. Its specific heat is 0.0559. What is its atomic weight?

8. 21.94 gm. of the bromide of a metal were decomposed yielding 5.94 gm. of the metal. The specific heat of the metal is 0.0559. What is its atomic weight? (Equiv. wt. of bromine = 80.)

Chapter XII

FORMULAE AND EQUATIONS

1. What weights of (a) potassium chlorate, and (b) potassium nitrate, would, when heated, give off one litre of oxygen, measured at S.T.P.?



2. What volume of hydrogen, measured at 12° C. and 750 mm. pressure, would be obtained by dissolving 3.5 gm. of aluminium in hydrochloric acid?

3. What volume of oxygen, measured at 15° C. and 745 mm. pressure, would be obtained by heating 20 gm. of mercuric oxide?

4. The percentage composition of a compound is: magnesium 20, sulphur 26.7, oxygen 53.3. What is its formula?

5. The percentage composition of a compound is: iron 34.5, chlorine 65.5. What is its simplest formula? If its vapour density ($H = 1$) is 162.5, what is its molecular formula?

6. The percentage composition of a compound is: calcium 40, carbon 12, oxygen 48. What is its simplest formula?

7. The percentage composition of a compound is: nitrogen 26.2, hydrogen 7.4, chlorine 66.4. What is its simplest formula?

8. The percentage composition of a compound is: lead 62.6, nitrogen 8.4, oxygen 29.0. What is its simplest formula?

9. 0.723 gm. of the hydrated chloride of a metal on heating yielded 0.365 gm. of the anhydrous salt. The molecular weight of the anhydrous chloride is 110. How many molecules of water of crystallisation are present in the hydrated salt? [Cambridge.]

10. A compound has the following percentage composition: copper 25.4, sulphur 12.8, oxygen 25.7, water 36.1. What is its simplest formula?

11. The percentage composition of a compound is: carbon 12.75, hydrogen 2.12, bromine 85.1. Its vapour density ($H = 1$) is 94. What is its (a) simplest formula, (b) molecular formula?

Chapters XV and XVI

ACIDS, BASES AND SALTS

1. Starting with sulphuric acid, describe three distinct methods by which specimens of zinc sulphate crystals can be obtained.

What is meant by the terms: *acid*, *base*, *salt*, *basicity*?

[London.]

2. What do you understand by the terms: *normal salt*, *acid salt*, *basic oxide*, *bi-valent metal*?

Give two examples of each.

[Cambridge.]

3. What are the distinctive properties of acids and alkalis?

Explain what is meant by neutralisation and describe in detail how you would prepare a specimen of sodium hydrogen sulphate. [Cambridge.]

4. 9.5 litres of hydrogen chloride, measured at 17° C. and 750 mm. pressure, are dissolved in water, the resulting solution exactly neutralised by means of sodium hydroxide and the whole evaporated to dryness. What is the solid product obtained and how much does it weigh? [London.]

5. How would you show *experimentally* that hydrochloric acid is a monobasic acid and sulphuric acid is a dibasic acid? [Cambridge.]

6. A solution of an acid having a molecular weight of 150 was neutralised with a standard solution of sodium hydroxide. The concentration of the acid was 10 gm. per litre, and that of the sodium hydroxide was 4.55 gm. per litre. 25 c.c. of the solution of the acid neutralised 29.3 c.c. of the solution of the base. What is the basicity of the acid? [Cambridge.]

7. 0.5 gm. of a sample of zinc containing zinc oxide gave on solution in hydrochloric acid 170 c.c. of hydrogen measured at 17° C. and 750 mm. Calculate the percentage of zinc in the sample. Sketch and describe an apparatus which would be suitable for this experiment. [Cambridge.]

8. 2.205 gm. of a hydrated dibasic acid required 35 c.c. of normal sodium hydroxide for complete neutralisation. When 1.01 gm. of the hydrated acid was heated to constant weight, 0.72 gm. of the anhydrous acid was obtained. How many molecules of water of crystallisation does the acid contain? [Cambridge.]

9. What do you understand by *double decomposition*? Under what circumstances can it occur?

10. What is the equivalent weight of (a) an acid, and (b) a base?

11. How would you convert barium nitrate into (a) barium chloride, (b) barium sulphate?

Chapter XVII

THE HALOGENS

1. Describe briefly two methods of obtaining chlorine from common salt. How would you show that the latter is a compound of sodium and chlorine? [Oxford.]

2. Describe the preparation from common salt of a solution of hydrogen chloride. [Cambridge.]

3. Describe the action of chlorine on (a) cold potassium hydroxide solution, (b) hot potassium hydroxide solution, (c) slaked lime.

4. What reactions occur when chlorine water is exposed for a length of time to direct sunlight? [London.]

5. Calculate the volume of chlorine, measured at 12°C . and 740 mm. pressure, which will react with the whole of the hydrogen generated by the solution in dilute sulphuric acid of 5 gm. of magnesium; also calculate the weight of the product. [London.]

6. Compare the properties of chlorine with those of bromine.

7. Give an account of the experiments and reasoning necessary to prove that the formula of hydrogen chloride is HCl . [Oxford and Cambridge.]

8. How are hydrogen bromide and hydrogen iodide prepared? Explain why it is impossible to prepare them by methods similar to that commonly used for hydrogen chloride.

9. Describe experiments that show that chlorine is more active than bromine and iodine.

10. Explain the sublimation of iodine.

Chapter XVIII

CARBON AND ITS OXIDES

1. How would you prove that graphite is an allotropic form of carbon? [Oxford and Cambridge.]

2. If you were given a mixture of carbon monoxide and carbon dioxide, how would you prepare a specimen of each of these gases in a state of purity? [Oxford and Cambridge.]

3. Describe clearly, with a sketch of the apparatus used, how you would show that carbon dioxide contains its own volume of oxygen. [London.]

4. Describe, with a sketch, how you would prepare and collect pure dry carbon monoxide.

Explain how you would convert some of this gas completely into carbon dioxide. How would you prove that the change is complete? [London.]

5. 3 litres of dry carbon monoxide, measured at s.t.p., were passed over heated copper oxide and the resulting carbon dioxide absorbed in potash bulbs. Calculate the loss of weight of the copper oxide and the gain in weight of the potash bulbs. [Cambridge.]

6. What is the action of (a) carbon dioxide, (b) steam upon red hot carbon, and what is the importance of these reactions for technical purposes? [Cambridge.]

7. What are the causes of the hardness of many natural waters? How may hard water be softened if the hardness is (a) temporary, (b) permanent? Discuss fully the chemical changes involved. [Cambridge.]

8. How would you test a given sample of oxygen to see if it contained (a) carbon dioxide, (b) nitrogen? Describe the apparatus you would employ to determine the percentages by volume of these impurities if present.

[Cambridge.]

9. Give reasons for considering that carbon monoxide is (a) a reducing agent, (b) an unsaturated compound.

Chapter XIX

HYDROCARBONS

1. Describe the preparation of methane. What reasons are there for considering that methane is a saturated compound?

How could you distinguish between methane and carbon monoxide?

2. Ethylene is said to be an unsaturated compound; give reasons for this statement. How can it be converted into a saturated hydrocarbon?

3. How can acetylene be prepared from calcium carbide? What are its practical uses?

Why do you consider that it is an unsaturated compound?

4. How would you distinguish between methane and a mixture of ethylene with twice its volume of hydrogen?

[Cambridge.]

5. What volume of oxygen would be necessary to burn completely three litres of methane, all the volumes being measured at the same temperature and pressure?

[Cambridge.]

6. In three separate experiments, 5 c.c. of (a) methane, (b) ethylene, (c) acetylene were each mixed with 20 c.c. of oxygen and the mixtures exploded by electric sparks. What is the composition by volume of the products of each experiment, all the measurements being made at a fixed temperature above 100°C . and at the same pressure?

[Cambridge.]

7. Determine the percentage composition by volume of a mixture of hydrogen and acetylene, 10 c.c. of which required 13 c.c. of oxygen for complete combustion.

[Cambridge.]

Chapter XXI

AMMONIA

1. Describe a process of preparing ammonia from nitrogen.

2. How would you prepare and collect some jars of dry ammonia? Draw a sketch of the apparatus. Describe an experiment by which you could obtain a specimen of nitrogen from ammonia.

[N.U.]

3. How would you prepare a strong solution of ammonia in water? How would you prepare from your solution (a) nitrogen, (b) crystallised ammonium nitrate? [Oxford and Cambridge.]

4. What experiments would you perform to show that ammonia contains hydrogen?

5. Describe and explain an experiment which proves that the atomic proportions of nitrogen and hydrogen in ammonia are as 1 : 3.

6. A sample of sodium sulphate containing a small proportion of ammonium sulphate is warmed with caustic soda solution. What will be produced and how can it be detected?

7. What changes take place when ammonia is passed (a) through a red-hot iron tube, (b) into dilute sulphuric acid, and when a stream of chlorine is passed into an aqueous solution of ammonia? [London.]

Chapter XXII

ACIDS AND OXIDES OF NITROGEN

1. How would you prepare from sodium nitrate a specimen of nitric acid? How would you prove that nitric acid (a) contains oxygen, (b) is an oxidising agent? [Oxford and Cambridge.]

2. If you were provided with some solid ammonium nitrate, how would you use it to prepare specimens of (a) nitric acid, (b) nitrogen, (c) ammonia? [Oxford and Cambridge.]

3. Describe carefully two experiments you would make to distinguish between common salt and nitre. [London.]

4. Describe the action of nitric acid upon (a) copper, (b) hydrochloric acid, (c) a solution of ferrous sulphate containing sulphuric acid. [Cambridge.]

5. Describe, with a sketch of the apparatus used, the preparation and collection of a few jars of nitric oxide.

How would you show that nitric oxide contains both nitrogen and oxygen?

6. Describe the preparation of nitrous oxide. Compare and contrast the properties of the gas with those of nitric oxide. [Cambridge.]

7. 0.621 gm. of an oxide of nitrogen yielded 0.290 gm. of nitrogen when heated with iron. Deduce the formula of the oxide of nitrogen. [Cambridge.]

8. Describe a method for determining the volume of nitrogen which can be obtained by decomposing a known volume of nitrous oxide. [Cambridge.]

9. Assuming that one molecule of nitric oxide can be obtained from one molecule of potassium nitrate, calculate the volume of nitric oxide (measured at s.t.p.) which can be obtained from 1 gm. of potassium nitrate. [Cambridge.]

10. In what respects would a mixture of two volumes of nitrogen and one volume of oxygen differ from nitrous oxide? [London.]

Chapter XXIV

SULPHUR AND ITS COMPOUNDS

1. Starting from roll sulphur, how would you prepare

- (a) rhombic crystals of sulphur,
- (b) monoclinic (prismatic) crystals of sulphur,
- (c) plastic sulphur?

Mention two other elements which, like sulphur, exist in more than one variety. [Cambridge.]

2. Describe the preparation of a few jars of dry sulphur dioxide. Give an account of the experiments and reasoning necessary to prove that the formula of this gas is SO_2 . [Oxford and Cambridge.]

3. How may sulphur dioxide be converted into sulphur trioxide? What is the action of sulphur dioxide with hydrogen sulphide? [Oxford and Cambridge.]

4. When sulphur is heated in air sulphur dioxide is formed. How would you prepare a pure specimen of sulphur dioxide by this method? [Cambridge.]

5. What reagent would you employ in order to remove sulphur dioxide from hydrogen?

6. Describe the properties of sulphuric acid. Why is this compound regarded as (a) an acid, (b) a dibasic acid? [Oxford and Cambridge.]

7. Given a supply of pure sulphur, explain carefully how you would prepare from it a moderately pure aqueous solution of sulphuric acid.

Describe and explain what happens when such a solution is added to (a) metallic magnesium, (b) a solution of lead nitrate, (c) chalk.

[London.]

8. What is understood by the term "catalytic agent"? Describe two processes in which catalysis is employed either on a large or small scale. [Cambridge.]

9. Write a short account of the action of acids on metals, pointing out how it varies with the acid, the metal and any other factors. [Oxford.]

10. Describe the preparation and properties of hydrogen sulphide. How would you prove that the formula of the gas is H_2S ? [Oxford and Cambridge.]

11. What reactions take place when sulphuretted hydrogen is passed into aqueous solutions of (a) caustic soda, (b) copper sulphate, (c) chlorine, (d) nitric acid? [Oxford and Cambridge.]

12. How would you determine experimentally the composition by volume of a mixture of sulphuretted hydrogen with hydrogen? [London.]

13. Name three substances which are commonly employed for drying gases. State, giving your reasons, which of these you would select in order to dry the following gases: ammonia, hydrogen sulphide, hydrogen chloride, carbon dioxide, and sulphur dioxide. Describe briefly how you would collect each gas after drying it.

Chapter XXV

PHOSPHORUS

1. Contrast the properties of red and white phosphorus.
2. In what forms does the farmer supply phosphates to the soil.
3. State two tests by which a phosphate may be identified.
4. What would be the result of heating common salt with phosphoric acid? Does this prove that phosphoric acid is a stronger acid than hydrochloric acid?
5. Describe the preparation of one of the chlorides of phosphorus. For what purpose is it used in chemistry?
6. Compare the properties of ammonia and phosphine.

Chapter XXVI

SILICON

1. Name three varieties of silica which are found in nature.

State some purposes for which silica is often employed and indicate the particular properties on which these uses depend.

State fully the reasons for regarding silica as an acid-forming oxide.

[London.]

Chapter XXVII

REVERSIBLE ACTIONS

1. What experiments would you make in order to show the reversibility of the reactions between (a) iron and steam, and (b) calcium carbonate, water and carbon dioxide?

2. What changes take place when nitrogen peroxide is heated from -11°C. to 150°C. and how are they explained?

3. What experiments can be made to show that ammonium chloride dissociates when vaporized?

Chapter XXX

OXIDATION AND REDUCTION

1. Explain the terms *reducing agent*, *oxidising agent*.

Classify the following under these heads, giving experimental evidence in support of your statements: chlorine, carbon monoxide, sulphur dioxide, nitric acid. [London.]

2. How would you oxidise (a) hydrogen chloride, (b) sulphur, (c) ferrous sulphate? [Oxford and Cambridge.]

3. How would you oxidise (a) sulphur dioxide to sulphur trioxide, (b) lead sulphide to lead sulphate? [Cambridge.]

4. Explain why the conversion of ferrous chloride into ferric chloride is regarded as a case of oxidation.

5. Describe the preparation of hydrogen peroxide. What is the action of this compound on (a) lead sulphide, (b) acidified potassium iodide, (c) silver oxide? [Oxford and Cambridge.]

6. By what tests can a solution of hydrogen peroxide be distinguished from water?

7. How is ozonised oxygen obtained? In what respects does this gas differ from ordinary oxygen? How can it be shown that (a) ozone is composed of oxygen atoms only, (b) its molecular weight is greater than that of oxygen? [Oxford and Cambridge.]

8. Name two reactions in which potassium permanganate acts as an oxidising agent.

Chapter XXXII

METALS

1. State four properties, of which one must be chemical, which are characteristic of metals. [N.U.]

2. Explain how you would prepare (a) sodium carbonate from caustic soda, (b) caustic soda from sodium carbonate.

3. How is sodium bi-carbonate prepared on a large scale?

4. How can sodium carbonate be prepared from sodium bi-carbonate? How can sodium carbonate be converted into sodium bi-carbonate?

5. How can caustic soda be prepared from common salt? What other substances are produced at the same time?

Chapter XXXIII

INDUSTRIAL METALS

1. Starting from black copper oxide, give two distinct methods for obtaining a sample of copper. State six of the more important properties of metallic copper.

Given metallic copper, how would you prepare (a) dry crystals of copper sulphate, (b) a dry specimen of ordinary copper carbonate? [London.]

2. Describe how you would prepare from litharge (PbO) (a) metallic lead, (b) crystalline lead chloride, (c) crystalline lead nitrate, (d) lead sulphide. [Cambridge.]

3. Describe briefly the reactions by which it is possible to obtain lead from galena (PbS). [N.U.]

4. Given supplies of copper nitrate and copper carbonate, how would you prepare two different specimens of copper oxide? Describe how you would use these different specimens to verify the Law of Definite Proportions. [N.U.]

5. Describe briefly, with examples, two general methods of preparing basic oxides.

6. How would you distinguish between (a) lead chloride and stannous chloride, (b) lead sulphate and zinc sulphate?

7. How can the anhydrous chlorides of (a) zinc and (b) magnesium be prepared?

ANSWERS TO QUESTIONS

Chaps. VI and VII. 2. 44. 3. 30. 4. 28. 5. 64. 6. 17. 7. 154.
8. 84. 9. 168. 10. 188.

Chap. VIII. 1. 14. 2. 35.5. 3. 32. 4. E.W.'s 63.50 and 31.75.
5. E.W.'s 200, 100. 6. E.W.'s 200.6, 100.3. 7. E.W.'s 18.66, 28.
8. E.W.'s 59.4, 29.7.

Chap. XI. 3. 56.2, 112.4. 4. 9.033, 27.1. 6. 1307 c.c., 3.77 gm. 7. 107.9.
8. 29.7, 118.8.

Chap. XII. 1. (a) 3.65 gm.; (b) 9.02 gm. 2. 4.607 l. 3. 1.113 l.
4. MgSO_4 . 5. FeCl_3 , Fe_2Cl_6 . 6. CaCO_3 . 7. NH_4Cl .
8. $\text{Pb}(\text{NO}_3)_2$. 9. 6. 10. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. 11. CH_2Br , $\text{C}_2\text{H}_4\text{Br}_2$.

Chaps. XV and XVI. 4. 23.04 gm. 6. 2. 7. 92.2 %. 8. 2.

Chap. XVII. 5. 4.94 l., 15.0 gm.

Chap. XVIII. 5. 2.143 gm., 5.893 gm.

Chap. XIX. 5. 6 l. 6. (a) 10 c.c. O_2 , 5 c.c. CO_2 , 10 c.c. steam;
(b) 5 c.c. O_2 , 10 c.c. CO_2 , 10 c.c. steam; (c) 7.5 c.c. O_2 , 10 c.c. CO_2 ,
5 c.c. steam. 7. 60 % H_2 , 40 % C_2H_2 .

Chap. XXII. 7. Simplest formula NO . 9. 221.8 c.c.

Atomic Weights

		Symbol	Atomic weight		Symbol	Atomic weight
Aluminium	...	Al	26.97	Molybdenum	Mo	96.0
Antimony	...	Sb	121.76	Neodymium	Nd	144.3
Argon	...	A	39.9	Neon	Ne	20.18
Arsenic	...	As	74.93	Nickel	Ni	58.69
Barium	...	Ba	137.36	Niton (radium emanation)	Nt	222.4
Beryllium	...	Be	9.02	Nitrogen	N	14.008
Bismuth	...	Bi	209.0	Osmium	Os	190.8
Boron	...	B	10.82	Oxygen	O	16.00
Bromine	...	Br	79.92	Palladium	Pd	106.7
Cadmium	...	Cd	112.41	Phosphorus	P	31.02
Caesium	...	Cs	132.81	Platinum	Pt	195.2
Calcium	...	Ca	40.07	Potassium	K	39.10
Carbon	...	C	12.00	Praseodymium	Pr	140.9
Cerium	...	Ce	140.13	Radium	Ra	225.97
Chlorine	...	Cl	35.46	Rhodium	Rh	102.9
Chromium	...	Cr	52.01	Rubidium	Rb	85.45
Cobalt	...	Co	58.95	Ruthenium	Ru	101.7
Columbium	...	Cb	93.3	Samarium	Sa	150.3
Copper	...	Cu	63.57	Scandium	Sc	45.1
Dysprosium	...	Dy	162.5	Selenium	Se	79.2
Erbium	...	Er	167.7	Silicon	Si	28.06
Europium	...	Eu	152.0	Silver	Ag	107.88
Fluorine	...	F	19.0	Sodium	Na	22.997
Gadolinium	...	Gd	157.3	Strontium	Sr	87.63
Gallium	...	Ga	69.72	Sulphur	S	32.06
Germanium	...	Ge	72.6	Tantalum	Ta	181.4
Gold	...	Au	197.2	Tellurium	Te	127.5
Hafnium	...	Hf	178.6	Terbium	Tb	159.2
Helium	...	He	4.00	Thallium	Tl	204.39
Holmium	...	Ho	163.5	Thorium	Th	232.12
Hydrogen	...	H	1.008	Thulium	Tm	169.4
Indium	...	In	114.8	Tin	Sn	118.7
Iodine	...	I	126.93	Titanium	Ti	47.9
Iridium	...	Ir	193.1	Tungsten	W	184.0
Iron	...	Fe	55.84	Uranium	U	238.14
Krypton	...	Kr	82.92	Vanadium	V	50.95
Lanthanum	...	La	138.9	Xenon	Xe	130.2
Lead	...	Pb	207.22	Ytterbium		
Lithium	...	Li	6.94	(Neoytterbium)	Yb	173.5
Lutecium	...	Lu	175.0	Yttrium	Yt	88.92
Magnesium	...	Mg	24.32	Zinc	Zn	65.38
Manganese	...	Mn	54.93	Zirconium	Zr	91.22
Mercury	...	Hg	200.6			

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	92
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6

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	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	5	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9470	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2
01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2
03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2
04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	1	2	2
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	1	2	2
06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	1	2	2
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	1	2	2
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	1	2	2
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	1	2	2
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	1	2	2
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	1	1	2	2
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	1	1	2	2
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	1	1	2	2
14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	1	1	2	2
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	1	1	2	2
16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	1	1	2	2
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	1	1	2	2
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	1	1	2	2
19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	1	1	2	3
20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	1	1	2	3
21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	1	1	2	3
22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	1	1	2	3
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	1	1	2	3
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	1	1	2	3
25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	1	1	2	3
26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	1	1	1	2	3
27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	1	1	1	2	3
28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	1	1	1	2	3
29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	1	1	1	2	3
30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	1	1	1	2	3
31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	1	1	1	2	3
32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	1	1	1	2	3
33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	1	1	1	2	3
34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	1	1	1	1	2	3
35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	1	1	1	1	2	3
36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	1	1	1	1	2	3
37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	1	1	1	1	2	3
38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	1	1	1	1	2	3
39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	1	1	1	1	2	3
40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	1	1	1	1	2	3
41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	1	1	1	1	2	3
42	2630	2636	2642	2648	2655	2661	2667	2673	2679	2685	1	1	1	1	1	1	2	3
43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	1	1	1	1	2	3
44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	1	1	1	1	2	3
45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	1	1	1	1	2	3
46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	1	1	1	1	2	3
47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	1	1	1	1	2	3
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	1	1	1	1	2	3
49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	1	1	1	1	2	3

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	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
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